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ISOTOPE SEPARATION BY CHEMICAL EXCHANGE PROCESS

FINAL TECHNICAL REPORT

PROJECTS E26-674 & E26-646

By

Alfred Schneider
Project Director

Submitted to

Department of Energy
Oak Ridge Operations
P. O. Box E
Oak Ridge, TN 37830

February 1987

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With the U.S. Department of Energy

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ABSTRACT

The feasibility of a chemical exchange method for the separation of the isotopes of europium was demonstrated in the system $\text{EuCl}_2\text{-EuCl}_3$. The single stage separation factor, α , in this system is 1.001 or 1.0005 per mass unit. This value of α is comparable to the separation factors reported for the $\text{U}^{4+} - \text{U}^{6+}$ and $\text{U}^{3+} - \text{U}^{4+}$ systems. The separation of the ionic species was done by precipitation of the Eu^{2+} ions or by extraction of the Eu^{3+} ions with HDEHP. Conceptual schemes were developed for a countercurrent reflux cascades consisting of solvent extraction contactors. A regenerative electrocel, combining simultaneous europium reduction, europium oxidation with energy generation, and europium stripping from the organic phase is described.

1. INTRODUCTION

The definition of the term "isotopes", introduced early in this century by F. Soddy, implies that atoms of the same element but of different mass have identical chemical properties. Yet, very slight differences in chemical properties have been exploited to achieve the separation of isotopes of the same element.

Many successful methods have been developed for the separation of isotopes, utilizing slight differences in physical or chemical properties. The first successful separation of the isotopes of neon by F. W. Aston (gaseous diffusion, 1913, and mass spectroscopy, 1919) and the introduction in 1932, of the concept of the separation cascade by G. Hertz were milestones in the evolution of an entirely new industry devoted to the separation of the isotopes of elements ranging from hydrogen to uranium.

H. C. Urey succeeded during the early 1930's to separate by chemical exchange reactions the isotopes of hydrogen, carbon, nitrogen, and sulfur, and numerous applications based on the chemical exchange separation principle were developed subsequently. The highly successful GS process for the production of heavy water utilizes the temperature-dependent equilibrium constant for the deuterium exchange reaction between H_2O and H_2S . Plants with annual production rates of hundred of thousands of tons of heavy water have been built in several countries. Successful processes were also developed and operated on a sizeable scale for the separation of lithium and boron isotopes.

An opinion which prevailed until the nineteen seventies held that chemical exchange processes were practical only for the separation of the isotopes of the light elements and that different processes, generally based on slight differences in physical or optical properties, should be investigated for the heavier elements. The outstanding success of the uranium enrichment processes based on gaseous diffusion, gas centrifugation, and, more recently, laser-induced ionization contributed to a general lack of interest in the investigation of chemical exchange processes for all but the lightest elements.

Notwithstanding the finding by Woodard¹ in 1948 that an isotope effect exists in the exchange reaction between ions of tetra- and hexavalent uranium, the scientific community was surprised when French² and Japanese³ investigators reported promising results for uranium enrichment processes based on chemical exchange reactions.

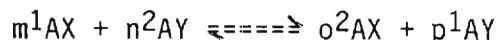
The separation of the isotopes of the elements of the lanthanide series has been achieved on a very small scale, using electromagnetic, photoionization, and chromatographic methods. In the course of this project, it was demonstrated that an isotope effect exists in the exchange reaction between ions of di- and trivalent europium and that counter-current solvent extraction could be used for the separation of europium and, presumably, other elements.

Isotope separation processes are quite energy-intensive and chemical exchange processes also consume considerable energy. The ionic chemical exchange reactions on which the French CHEMEX process for uranium enrichment and the europium isotope separation investigated in this study are based require considerable energy to reverse the valence of the ions at the bottom and the top of the cascade to allow for the necessary reflux. A new concept was proposed for a regenerative redox cell which could result in considerable savings of electrical energy by exploiting the unique requirement for oxidizing and reducing chemical species of the same element but of different isotopic composition.

2. THE SEPARATION OF ISOTOPES BY CHEMICAL EXCHANGE

2.1 Fundamentals

A chemical exchange reaction involving isotopes 1A and 2A of element A present in two different compounds AX and AY can be represented by



The relationship at equilibrium is given by the equilibrium constant K:

$$K = \frac{[^2AX]^o [^1AY]^p}{[^1AX]^m [^2AY]^n}$$

For simple stoichiometry,

$$K = \frac{[{}^2\text{AX}]}{[{}^1\text{AX}]} \bigg/ \frac{[{}^2\text{AY}]}{[{}^1\text{AY}]} = \alpha$$

where the quotients in the numerator and denominator are the relative isotope ratios in compounds AX and AY and α is the separation factor. The equilibrium constant is equal to the separation factor, provided the following two criteria are met:

The chemical species involved in the exchange reaction must contain or exchange only one atom of the isotopic element.

There must be no net transfer of the two chemical species across the boundaries of the two phases.

The separation factor α will be greater than one if the isotope ratios differ. The degree by which α differs from one is an indication of the utility of a chemical exchange reaction in achieving a separation of the isotopes. Examples of several chemical exchange reactions are shown in Figure 1.

It should be noted that for a chemical exchange reaction to be of practical value, compounds AX and AY must be amenable to a physical separation after equilibrium has been achieved. This would be the case if AX were a liquid and AY a gaseous compound or if AX and AY were immiscible liquids with good mass transfer rates of the different isotopes between the two phases.



$$\alpha = \frac{[^2\text{AX}][^1\text{AY}]}{[^1\text{AX}][^2\text{AY}]} = \frac{[^2\text{AX}]/[^1\text{AX}]}{[^2\text{AY}]/[^1\text{AY}]}$$

EXAMPLES:



$$\alpha = 2.37 \text{ (25}^\circ\text{C)}$$



$$\alpha = 1.001$$



$$\alpha > 1.0027$$

FIGURE 1. CHEMICAL EXCHANGE REACTIONS

A single separating unit is the designation for the contacting device in which equilibrium is achieved. Units are arranged in cascades and, if dictated by flow requirements, several units may be operated in parallel at a given location of the cascade.

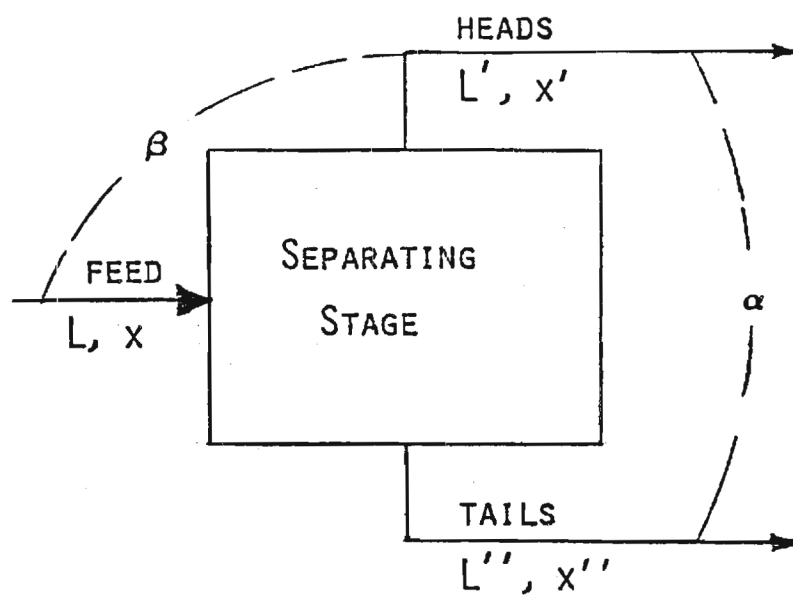
The relations around a separating unit and for a cascade are shown in Figures 2 and 3.

Cascades are of different types, depending on the flow arrangements between various stages. Two common types, the simple cascade and the countercurrent reflux cascade, are shown in Figure 4.

2.2. Theory

Since Soddy and Hyman discovered, in 1912, the isotopes of lead, it was generally assumed that there was little difference in the chemical behavior of the isotopes of the same element. However, isotopes of a given element may show some quantitative differences in chemical reaction equilibrium and reaction rate or in the preferential stability in various chemical compounds of the element.

Clewett and Schaap⁴ explained this "isotope effect" in a chemical exchange reaction as a slight difference of affinity of the isotopes for a given molecule or complex due to minor variances in the internal energies (mainly the vibrational energy)



$$\alpha = \frac{x'}{x''} \cdot \frac{1 - x''}{1 - x'}$$

$$\beta = \frac{x'}{x} \cdot \frac{1 - x}{1 - x'} = \dots = \sqrt[n]{\frac{x^n}{x^0} \cdot \frac{1 - x^0}{1 - x^n}}$$

$$\theta = \frac{L'}{L} = \frac{x - x''}{x' - x''}$$

$$\alpha - 1 = \frac{\beta - 1}{(1 - \theta) - \theta(1 - x')(\beta - 1)}$$

FIGURE 2. SEPARATING STAGE RELATIONSHIPS

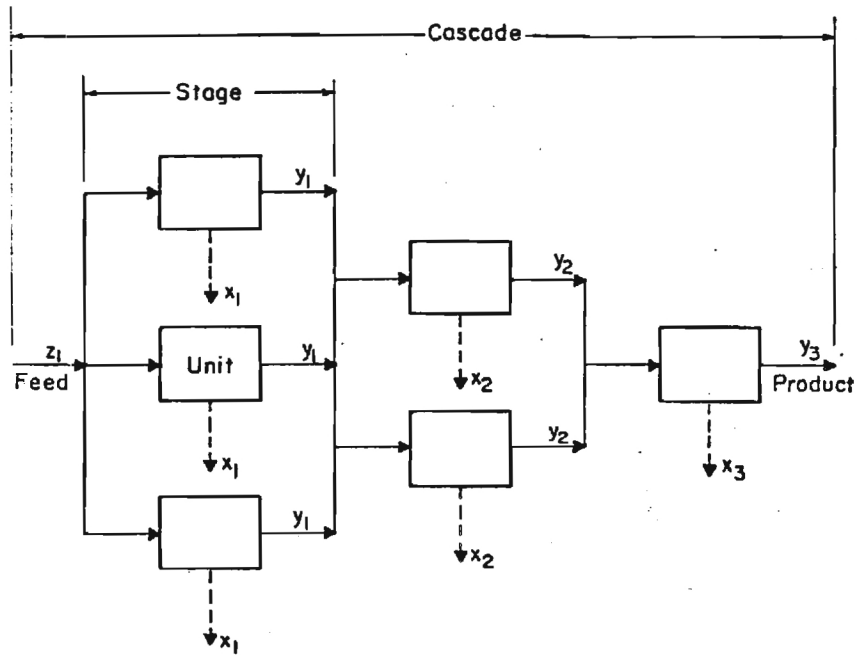
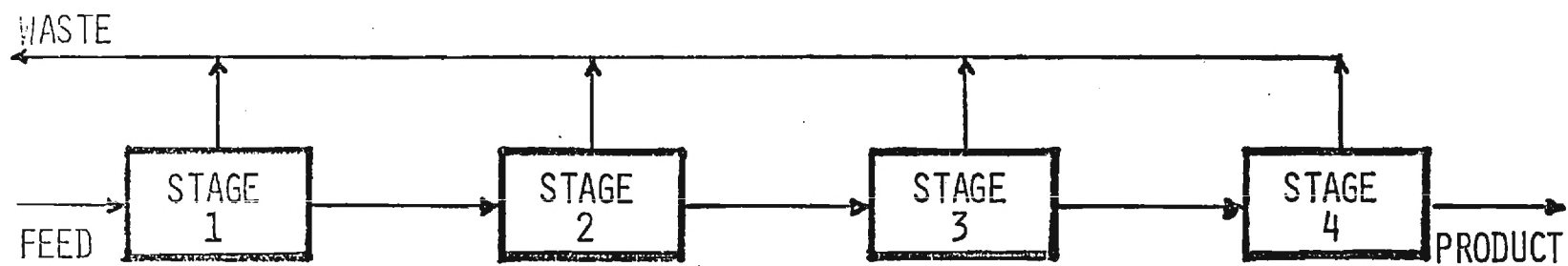
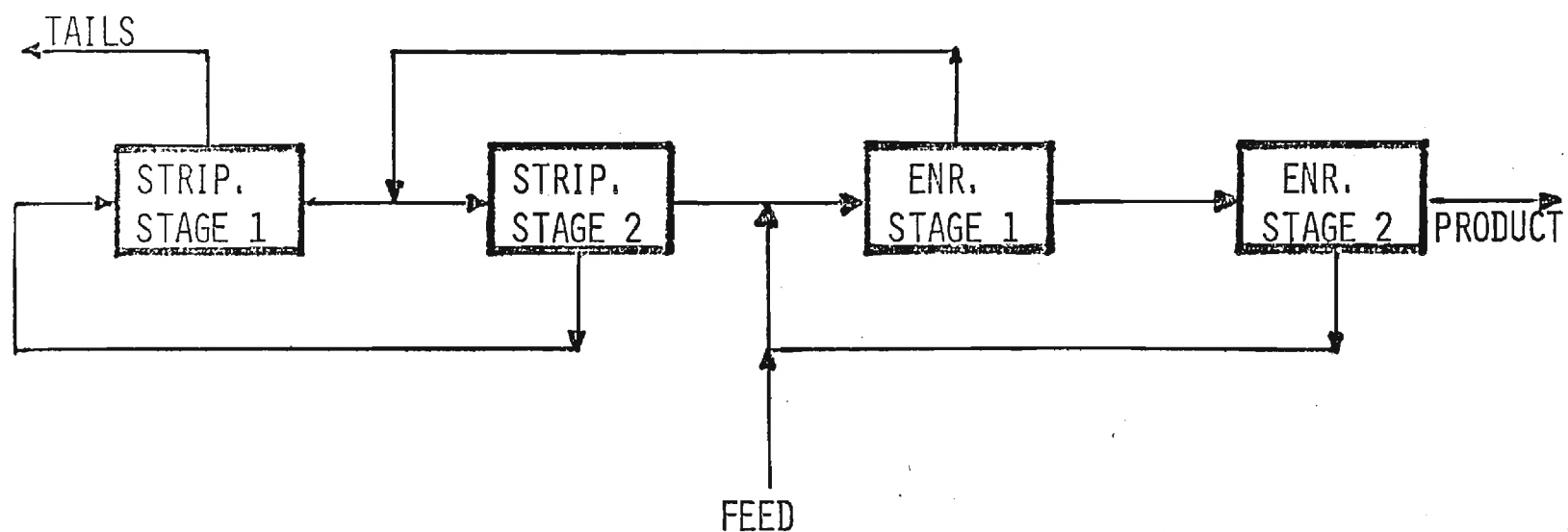


FIGURE 3. RELATIONS FOR A CASCADE



SIMPLE CASCADE



COUNTERCURRENT REFLUX CASCADE

FIGURE 4. CASCADE TYPES

of the molecule, the heavier isotope having a greater affinity for the molecular state and the lighter one tending to remain in a more dissociated state. Wahl and Bonner believed that the differences in chemical behavior of the isotopes were due to their differences in mass. The mass of the atoms in a molecule should affect both the velocity and vibrational energy of the molecule. If all molecules are at the same temperature, the heavier molecules have a lower velocity and, therefore, undergo fewer collisions. The heavier molecules also have less vibrational energy than the light molecules and this require more energy for dissociation. Molecules of different isotopes are also expected to undergo chemical transformation at different rates. Nearly always, the heavier molecule will react more slowly than the lighter molecule, partly because it undergoes fewer collisions and partly because more energy is required to excite it to the activated transition state.

According to Villani⁵ there are two types of properties that depend directly on mass and are thus usable for isotopic separations. One type is related to the "individual" diversity of movement of molecules of different masses (e.g., when the molecules are subject to a gravitational field or, in the case of ions, to an electrical field). The other type has to do with the varying "statistical" behavior of molecular species of differing masses (e.g., in a gaseous mixture in thermal equilibrium, the square of the mean velocity of the various molecules is inversely proportional to the square root of the mass).

The diverse statistical behavior of isotopic molecular species, to which we owe a separation effect, is often only indirectly connected with the diversity of their masses through the zero-point energies. Slight differences in the levels of such zero point energy affect the volatility, the constants of chemical equilibrium, the reaction speed, and other properties of the isotopic species.

The isotope effect in exchange reactions was studied by Urey and Rittenberg⁶ for the hydrogen and deuterium halides exchange reactions. Since then, equilibrium constants have been calculated for many isotopic exchange reactions, applying information obtained from molecular vibrational spectra. Blagg and Murphy⁷; Thode and Urey⁸; Hutchison, et al.⁹; Urey¹⁰, and Bigeleisen and Mayer¹¹ extended the equilibrium constant calculation based on molecular vibrational spectra to isotopic exchange reactions of the heavier elements. Babloyantz¹²; Boato, et al.^{13,14,15}; Oppenheim and Friedman¹⁶; Bigeleisen^{17,18}; Van Hook¹⁹, and Kakihana²⁰ expanded and developed the same subject into the study of the isotope effects on condensed phases, such as liquids and solids.

The isotope effect in exchange reactions can be expressed mathematically by utilizing the molecular vibrational theory based on quantum statistical mechanics and statistical thermodynamics. For example, the equilibrium constant K for the isotopic exchange reaction:



is given by the molecular partition function:

$$K = \frac{Q_{BX} / Q_{AX}}{Q_{BY} / Q_{AY}}$$

where A and B are the isotopes and X and Y are the chemical species bonded to them (X and Y do not include isotopes A and B). The classical representation of the molecular partition function is:

$$h^g Q = \frac{1}{S} \iiint \dots \iiint e^{-H(p,q)/kT} dp \dots dq,$$

where h is the Planck constant, g is the number of degrees of freedom of the molecule, S is the symmetry number, and H is the Hamiltonian of the momenta p and the coordinates q of the constituent atoms:

$$H = \sum_{i=1}^{3N} p_i^2 / 2M_i + V(q_i)$$

The integration over the p's leads to:

$$Q = \frac{1}{S} \prod_i \left(\frac{2\pi M_i kT}{h^2} \right)^{3/2} \times \iiint \dots \iiint e^{-\frac{V(q_i)}{kT}} dq_i$$

The potential energies for molecules differing only in isotopic constituents are alike. The ratio of the partition functions of two isotopic molecules is, therefore, seen to reduce to the inverse ratio of the symmetry number multiplied by the mass ratio of the different isotopes raised to three-halves power:

$$\frac{Q}{Q'} = \frac{S'}{S} \left(\frac{M}{M'} \right)^{3/2}$$

The ratio of the symmetry numbers, no matter what its value, will not lead to isotopic enrichment since it merely represents the relative probabilities of forming symmetrical and unsymmetrical molecules.

In calculating the equilibrium constant of isotopic exchanges the classical mass ratio $(M/M')^{3/2}$ is best omitted. This omission amounts to calculating the ratio of the equilibrium constants for the dissociation of the two isotopic molecules into atoms. Therefore, the ratio of the partition functions can be defined as follows:

$$f = \frac{Q}{Q'} \prod_i \left(\frac{M'_i}{M_i} \right)^{3/2} \times \left(\frac{S'}{S} \right) \text{ or } \left(\frac{S}{S'} \right) f = \frac{Q}{Q'} \prod_i \left(\frac{M'_i}{M_i} \right)^{3/2}$$

In classical mechanics $(S/S')f$ is equal to one. A value of one for $(S/S')f$ means there will be no separation of isotopes.

In quantum mechanics, the partition function may, as a first approximation, be written as the product of translational, rotational, and vibrational partition functions. The translational partition function is equal to the classical one at all temperatures. The rotational partition function, in all cases except hydrogen, is classical at room temperature. The form of the vibrational partition function, neglecting anharmonicity, is:

$$Q_{\text{vib}} = \prod_i \frac{e^{-u_i/2}}{1 - e^{-u_i}}$$

where

$$u_i = h \nu_i / k T$$

and the product is to be taken over the different vibrational frequencies ν_i of the molecule counting an n -fold degenerate frequency n times. At high temperatures or low u , Q_{vib} reduces to $\prod_i (1/u_i)$, which is identical with the classical expression. In

the quantity f , these limiting values as well as the rotational and the translational parts cancel, leaving only the ratio of the symmetry numbers.

The value of f depends upon the vibrations only and is of the form:

$$\frac{S}{S'} f = \prod_i \frac{u_i}{u'_i} \frac{e^{-u_i/2} / (1 - e^{-u_i})}{e^{-u'_i/2} / (1 - e^{-u'_i})}$$

The value of u'_i can be written as $u_i + \Delta u_i$, where the primed molecule is the lighter one. The Δu_i is always positive and

$$\frac{S}{S'} f = \prod_i \frac{u_i}{u_i + \Delta u_i} e^{\Delta u_i/2} \frac{1 - e^{-(u_i + \Delta u_i)}}{1 - e^{-u_i}}$$

If Δu_i is small, which is the case for everything except the isotopes of hydrogen, then

$$\frac{S}{S'} f = 1 + \sum_i \left\{ \frac{1}{2} - \frac{1}{u_i} + \frac{1}{(e^{u_i} - 1)} \right\} \Delta u_i$$

If, in addition, u_i itself is small, then

$$\frac{S}{S'} f = 1 + \sum_i \frac{\Delta u_i u_i}{12} = 1 + \sum_i \frac{\Delta(u_i)^2}{24} \cdot$$

Furthermore, the sum of the square of all the frequencies of a molecule has the form

$$4 \pi^2 \sum_i \nu_i^2 = \sum_{n=1}^N \frac{A_n}{m_n}$$

where the summation on the right side extends over all atoms in the molecule and the A's depend only on force constants. Then,

$$\Delta \sum_i \nu_i^2 = \frac{\Delta m}{m m'} \frac{1}{4 \pi^2} A$$

where A is the sum of the three restoring force constants corresponding to the displacement of the isotopic atom in three mutually perpendicular directions. If the central atom of mass M or M + ΔM is symmetrically surrounded by n identical atoms of mass m, an approximation is useful in the absence of a complete knowledge of the vibrational frequencies of the molecules

$$\frac{S}{S'} f = 1 + \frac{\Delta M m}{24 M^2} u_1^2 n$$

where $u_1 = hc\omega_1/kT$ and ω_1 is the total symmetric or "breathing frequency."

The equilibrium constant will be as follows:

$$K = \frac{Q_{BX}/Q_{AX}}{Q_{BY}/Q_{AY}} = \frac{f_X}{f_Y}$$

If the molecules contain only one atom of the element undergoing isotopic substitution, the separation factor will be equal to the equilibrium constant as the symmetry numbers cancel.

$$\alpha = \frac{(S/S')f_X}{(S/S')f_Y} = \frac{f_X}{f_Y} = K$$

Thus, if the proper vibrational frequency data are available, the separation factor can be calculated.

Statistical thermodynamics can provide the same result for the calculation of the reaction equilibrium constant.

The equilibrium constant K for a typical reaction



is

$$K = \frac{(C)^\gamma \cdot (D)^\delta}{(A)^\alpha \cdot (B)^\beta} \quad \text{and} \quad RT \ln K = -\Delta F$$

where ΔF is the algebraic sum of the free energy ($F = H - TS$) of the various components. For one mole of ideal gas,

$$F = H - TS = E + PV - TS = E + RT - TS.$$

$$E = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

where

$$Q = \sum_i g_i e^{-E_i/kT}$$

is the partition function for the system under consideration (g_i is the statistical weight of the energy level E_i).

$$S = R T \left(\frac{\partial \ln Q}{\partial T} \right)_V + R \ln \frac{Q}{N} + R$$

Therefore, the free energy F will be:

$$\Delta F = - RT \Delta \ln \frac{Q}{N},$$

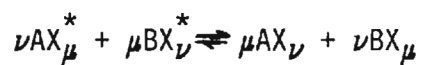
and K will become:

$$K = \frac{Q_C Q_D}{Q_A Q_B}$$

Since the total energy for each level can be broken down into the terms relating to the different degrees of freedom,

$$Q = Q_{\text{trans}} \cdot Q_{\text{rot}} \cdot Q_{\text{vibr}} \cdot Q_{\text{el}} \cdot Q_{\text{nuc}} \cdot e^{-E_0/kT}$$

For isotope-exchange reactions of the general type



in which X and X* are two isotopes of the same element, the equilibrium constant is:

$$K = \frac{(Q^{*}/Q)_{\nu AX_{\mu}}}{(Q^{*}/Q)_{\mu BX_{\nu}}}.$$

Neglecting anharmonicity, the zero-point energies differ only in the vibrational energy for isotopic molecules.

$$E_0 = 1/2 h \Sigma \nu$$

The Q^{*}/Q ratios can be written as:

$$\frac{Q^{*}}{Q} = \left(\frac{Q^{*}}{Q}\right)_{\text{trans.}} \left(\frac{Q^{*}}{Q}\right)_{\text{rot.}} \left(\frac{Q^{*}}{Q}\right)_{\text{vibr.}} e^{1/2(\Sigma u^{*} - \Sigma u)}$$

and

$$Q_{\text{trans.}} = \text{const} \times M^{3/2} T^{5/2} / p$$

in which M is the molecular weight and P is the pressure, and

$$Q_{\text{rot.}} = \text{const.} \times \frac{IT}{s}$$

for biatomic or linear polyatomic molecules (I is the moment of inertia, and s is the molecule's symmetry number, or

$$Q_{\text{rot.}} = \text{const.} \times \frac{(ABC)^{1/2} T}{s}$$

for nonlinear polyatomic molecules (A, B and C are the principal moments of inertia).

The partition function for the vibrational degrees of freedom is given by

$$Q_{\text{vibr.}} = \prod \left\{ \frac{1}{1 - e^{-u}} \right\}, \quad u = h c \omega / k T$$

in which the product is extended to all the basic frequencies of the molecule. With only a single basic frequency,

$$\frac{Q^*}{Q} = \frac{s}{s^*} \left(\frac{M^*}{M} \right)^{3/2} \frac{I^*}{I} \frac{e^{-u^*/2}}{1 - e^{-u^*}} \frac{1 - e^{-u}}{e^{-u/2}}$$

whereas for nonlinear polyatomic molecules, it becomes

$$\frac{Q^*}{Q} = \frac{s}{s^*} \left(\frac{M^*}{M} \right)^{3/2} \left(\frac{A^* B^* C^*}{ABC} \right) \prod \left\{ \frac{e^{-u^*/2}}{1 - e^{-u^*}} \frac{1 - e^{-u}}{e^{-u/2}} \right\}$$

where

$$\left(\frac{M^*}{M}\right)^{3/2} \left(\frac{A^*B^*C^*}{ABC}\right) = \Pi \left(\frac{u^*}{u}\right)$$

therefore

$$\frac{Q^*}{Q} = \frac{s}{s^*} \Pi \left\{ \frac{u}{u^*} \frac{e^{-u^*/2}}{1 - e^{-u^*}} \frac{1 - e^{-u}}{e^{-u/2}} \right\}$$

This equation is also applicable to biatomic molecules. It gives the same conclusions as quantum statistical mechanics.

From the calculations made by Mayer²⁶ the isotopic exchange equilibrium constant for the reaction:

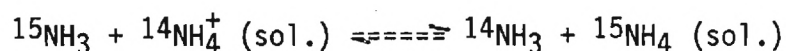


could be as much as 1.00122.

Chemical exchange reactions in which ions of the same element but of different valences are involved depend on a transfer of electrons from one atom to another. The rate of this transfer could determine the overall exchange rate and factors affecting the mechanism of electron transfer (hydration energy, stability of intermediate complexes, catalytic effect of other ions present, temperature, etc.) may have to be considered in the development of theoretical estimates.²¹

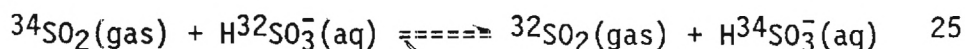
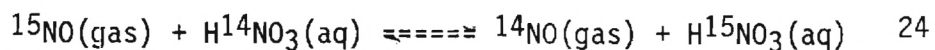
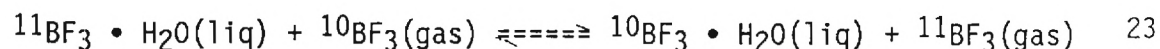
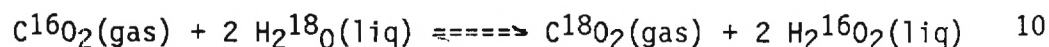
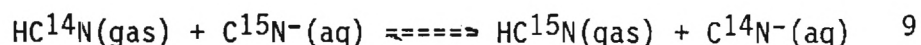
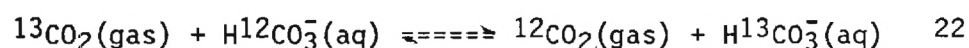
2.3. Applications

The first chemical exchange system for the enrichment of ^{15}N was reported by Thode and Urey in 1939:⁸



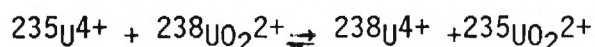
with an equilibrium constant of 1.035 at 298°K.

Following are some isotopic exchange reactions for a number of other low atomic weight elements:



Progress has been slower for heavier elements for which separation factors are much lower. Nevertheless, since many chemical exchange processes are thermodynamically reversible in

theory, energy would be required only for contacting of the phases and for reflux which would be applied only at the top and bottom of the cascade. In 1944, Mayer²⁶ showed, from first principles, that separation factors between 1.001 and 1.003 can be expected for ^{235}U - ^{238}U in the exchange equilibrium for the reaction:



Actual measurements made by Woodard¹, in 1948, confirmed this estimate. In numerous subsequent studies, either ion exchange resins or solvent extraction was used to provide the continuous separation of the two chemical forms of the element. Separation factors as high as 1.003 have been reported².

A review of previous studies showed that they fell short by at least one of four important requirements:

A single stage separation factor should be at least 1.001 and preferably 1.004.

The exchange reaction must take place between molecular species which exist separately in highly immiscible phases.

A method must exist for "refluxing" one element from one phase to the other.

Equilibrium must be rapidly established in the fundamental exchange reaction between the species in one phase and those in the other phase.

In 1976, Schneider²⁷ proposed a scheme for the isotopic enrichment between uranyl and uranous ions which utilized some of

the principles which led to the successful development of the electrochemical uranium plutonium partitioning method²⁸. The underlying principles of the scheme proposed by Schneider were:

The existence of an isotope effect in the $U^{4+} - U^{6+}$ equilibrium with a separation factor α between 1.001 and 1.004.

A significant difference between the distribution coefficients of U^{4+} and U^{6+} in the H_2O-HNO_3 - tributyl phosphate - $C_{12}H_{26}$ system.

The electrochemical or chemical reduction of U^{6+} , contained in a TBP, $C_{12}H_{26}$ solution dispersed in an aqueous HNO_3 solution, to U^{4+} which transfers rapidly to the aqueous phase.

The electrochemical or chemical oxidation of U^{4+} , contained in an aqueous HNO_3 solution, to U^{6+} .

Near quantitative stripping of U from TBP, $C_{12}H_{26}$ into water.

Near quantitative extraction of U from HNO_3 solution into TBP, $C_{12}H_{26}$.

Figure 5 illustrates the proposed basic mode of operation of one complete and two partial adjacent stages.

Compartment 1 represents a mixing chamber of a mixer-settler solvent extraction apparatus containing electrodes for the reduction of U^{6+} to U^{4+} . Initially, all the uranium entering 1 is in the oxidized U^{6+} state and, if sufficient HNO_3 is present, will extract largely into the organic TBP- $C_{12}H_{26}$ phase. Progressively, part of the uranium is reduced to U^{4+} which has a lower

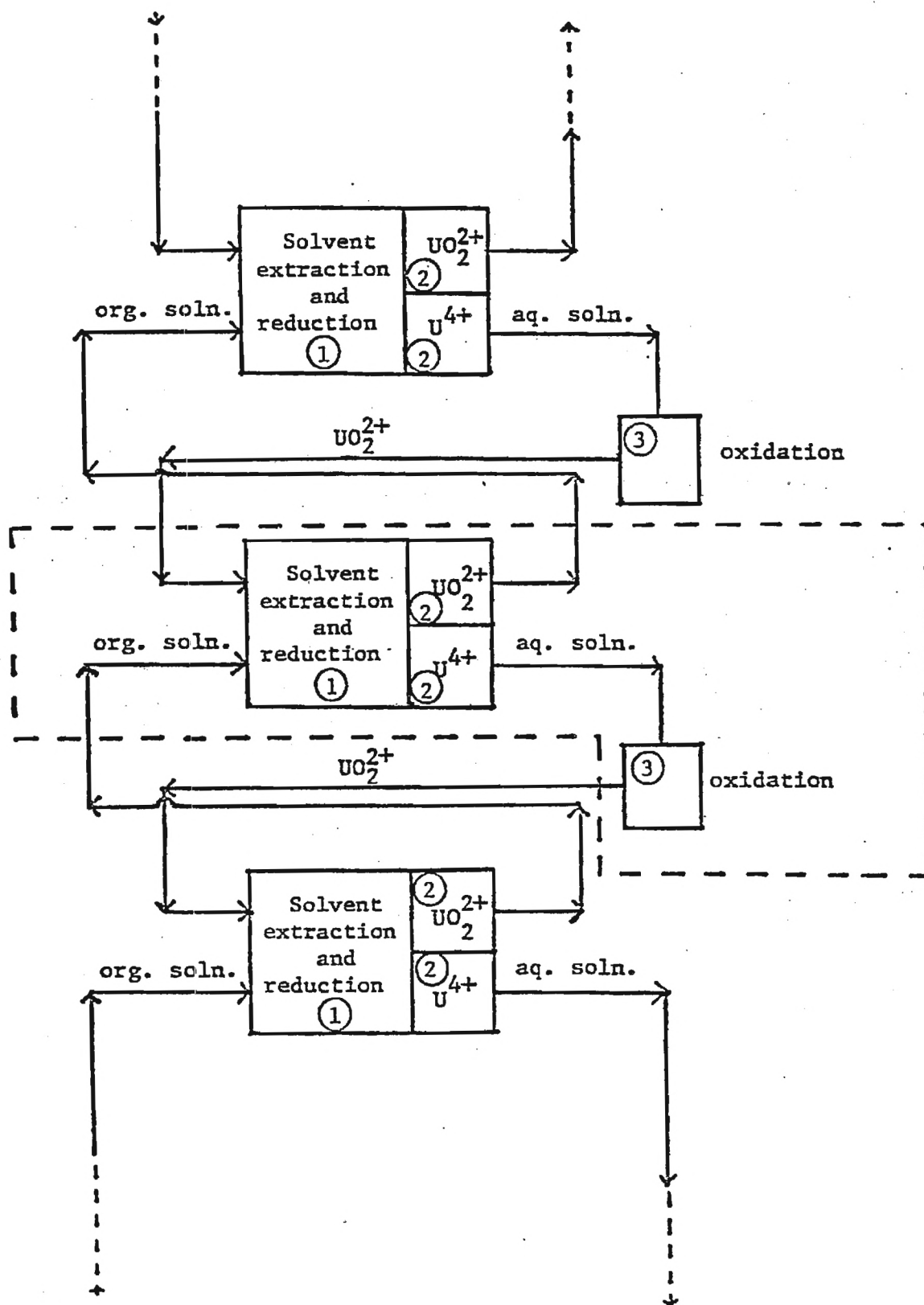


Figure 5. Stages of a Chemical Isotopic Separation Cascade

extractability and will transfer to the aqueous phase. Because of the isotope effect in the $U^{4+} - UO_2^{2+}$ system, the uranium in the aqueous phase will be slightly depleted in ^{235}U , while the uranium remaining in the organic phase will be slightly enriched in ^{235}U . Compartment 2 is a settling chamber which allows the lighter organic phase (containing UO_2^{2+}) to separate from the heavier aqueous phase (containing U^{4+}). The organic stream, containing uranium which had been slightly enriched, is directed to the mixing chamber 1 of the next higher stage, while the aqueous stream carrying the slightly depleted uranium is first oxidized (e.g. by contact with air) in chamber 3 and then introduced in the mixing chamber 1 of the next lower stage. Thus, a counter-current flow is established in which progressively higher enriched uranium moves "up" while a gradually more depleted uranium stream moves "down".

Figure 6 illustrates the manner in which many stages are arranged to form a cascade. The top and bottom stages for product and tails withdrawal also perform as reflux stages. The top stage consists of a stripping column and concentrator for the quantitative transfer of all the uranium from the organic to the aqueous phase. The uranium-free organic stream is directed to the bottom stage of the cascade. There, the uranium in the entering aqueous stream is transferred quantitatively to the recycled organic stream. The uranium-free aqueous solution can be recycled to the top stage.

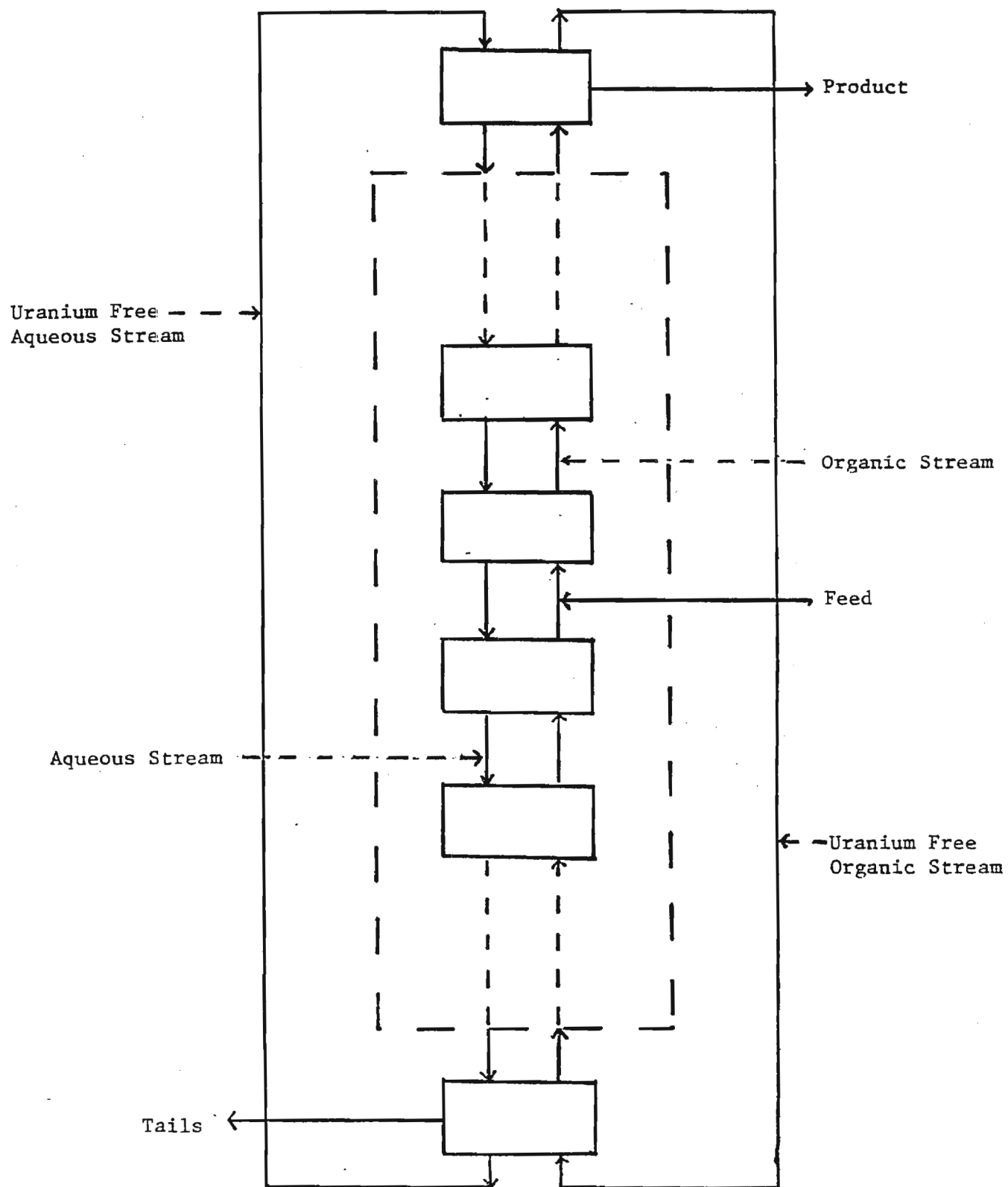


Figure 6. Chemical Isotopic Enrichment Cascade

Favorable exchange rates between the different valence species in the two phases could reduce or eliminate the need of intra-stage reduction or oxidation which would appreciably reduce the energy requirements of the separation process. This was subsequently confirmed and the French-developed CHEMEX process for uranium enrichment is, indeed, based on the countercurrent contacting of an organic solution containing uranium in a higher valence state with an aqueous solution containing uranium in a lower valence state.

Because of classification restrictions, it was not practical to pursue uranium enrichment studies within the confines of university research. For this reason, a search was made for an element which has the necessary chemical and physical properties to allow a fundamental investigation of the underlying principles of the isotope separation process by chemical exchange along the scheme proposed by Schneider.

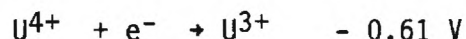
Europium, element number 63, was selected for the experimental investigation at Georgia Tech for the following reasons:

Natural europium consists of only two stable isotopes:
 ^{151}Eu - 47.82% and ^{153}Eu - 52.18%.

Divalent and trivalent europium ions exist in aqueous solutions and reduction and oxidation of these ions can be readily achieved by conventional chemical and electrochemical means.

Suitable solvent systems (e.g. acidic phosphoric and phosphonic esters) are available which permit an excellent separation of Eu^+ and Eu^{3+} ions.²⁻

The redox potentials of Eu^{3+} and U^{4+} are comparable:



The exchange rate between Eu^{2+} and Eu^{3+} in HCl solutions is relatively rapid.³⁰

Suitable analytical methods are available for the rapid determination of Eu^{2+} and Eu^{3+} ions.

The large difference between the thermal neutron absorption cross-section (^{151}Eu - $7,800 \pm 200$ barns, ^{153}Eu - 440 ± 25 barns), coupled with prominent gamma peaks in the nuclides resulting from neutron activation, may permit the determination of the isotopic composition of europium using a neutron activation method.

Several practical applications exist for separated europium isotopes (e.g. "custom tailored" burnable poisons for research reactors).

Research quantities of separated ^{151}Eu and ^{153}Eu are available from ORNL (Calutron - separated).

There are no previous reports on rare earths isotopic separation by chemical exchange.

The experimental results obtained in the course of this study show that the conjectures which led to the selection of europium were, generally, correct.

3. THE SEPARATION OF ISOTOPES OF THE LANTHANIDE ELEMENTS

Though many naturally occurring elements of the lanthanide group have more than one stable isotope, as shown in Table 1, only few investigations have been reported for isotopic separations.

TABLE 1

ISOTOPES OF LANTHANIDES

<u>ELEMENT</u>	<u>ATOMIC NO.</u>	<u>ATOMIC MASS</u>	<u>NUMBER OF ISOTOPES</u>	
			<u>NATURAL</u>	<u>ARTIFICIAL</u>
Ce	58	140.12	4	15
Pr	59	140.91	1	14
Nd	60	144.24	7	9
Pm	61		0	14
Sm	62	150.35	7	10
Eu	63	151.96	2	19
Gd	64	157.25	7	10
Tb	65	158.92	1	23
Dy	66	162.50	7	14
Ho	67	164.93	1	28
Er	68	167.26	6	10
Tm	69	168.93	1	17
Yb	70	173.04	7	9
Lu	71	174.97	2	21

Some of the lanthanide isotopes have very large capture cross-sections, as shown in Table 2. This must be taken into account in nuclear reactor reactivity calculations because of the buildup of fission products in the fuel. Certain lanthanide elements (Gd, Eu) have also found use as nuclear poisons, to control the reactivity of reactors and to prevent accidental criticality excursions in operations involving fissile materials.

Electromagnetic, photoionization with lasers, and liquid chromatographic methods have been reported for the separation of lanthanide isotopes. The application of chemical exchange methods has not been reported previously. A summary of lanthanide isotope separation studies is given in Table 3.

4. EXPERIMENTAL STUDIES WITH EUROPIUM

4.1 Objectives

The objectives of the first phase of this research project were:

The experimental determination of the isotopic separation factor for the Eu^{2+} - Eu^{3+} system under equilibrium and non-equilibrium (dynamic) conditions.

The verification by experimental and computer modeling methods of the operating stability of a solvent extraction cascade with a constant europium profile but with a cyclic variation in europium valence state.

The development of a conceptual design for a countercurrent enrichment cascade, based on the isotope effect in the Eu^{2+} - Eu^{3+} system, the use of a suitable solvent for the continuous separation of the Eu^{2+} and Eu^{3+} ions, the use of electrochemical or chemical reduction-oxidation to effect the cyclic transfer of europium between phases, and extensive stripping and extraction of europium on the top and bottom of the cascade for reflux and recycle of the carrier streams.

TABLE 2THERMAL NEUTRON CAPTURE CROSS-SECTIONS IN BARNs

<u>ISOTOPE</u>	<u>C.S.</u>
$^{145}\text{Pm}^*$	8,400
$^{148}\text{Pm}^*$	25,000
^{149}Sm	41,000
$^{151}\text{Sm}^*$	15,000
$^{155}\text{Eu}^*$	14,000
^{155}Gd	61,000
^{157}Gd	254,000
^{164}Dy	2,100
^{168}Yb	3,200

* Radioactive isotope

TABLE 3

SEPARATION OF LANTHANIDE ISOTOPES

ELECTROMAGNETIC	ORNL, INEL, KFA-JUELICH, AND OTHER SITES
PHOTOIONIZATION	N. V. KARLOV ET. AL. LEBEDEV PHYSICAL INST., MOSCOW, U.S.S.R. (1977) LASER ISOTOPE SEPARATION OF Nd, Sm, Eu, Gd, Dy, Er
CHROMATOGRAPHIC	H. SPECKER ET. AL. UNIVERSITAET BOCHUM, F.R.G. (1982) HPLC - ^{144}Sm AND ^{154}Sm O.S.F. = 1.06 HPLC - ^{141}Ce AND ^{143}Ce O.S.F. = 1.085 HPLC - ^{152}Eu AND ^{154}Eu O.S.F. = 1.03 LPLC - ^{140}Ce AND ^{142}Ce O.S.F. = 1.102 TLC - ^{152}Eu AND ^{154}Eu O.S.F. = 1.06
CHEMICAL EXCHANGE	A. SCHNEIDER, GEORGIA INSTITUTE OF TECHNOLOGY (1979) $\text{Eu}^{2+} - \text{Eu}^{3+}$ (SEPARATED BY SULFATE PRECIPITATION) S.S.F. FOR ^{151}Eu AND ^{153}Eu = 1.0006 $\text{Eu}^{2+} - \text{Eu}^{3+}$ (SEPARATED BY HDEHP EXTRACTION) S.S.F. = 1.0011 L. A. BOTTOMLEY, GEORGIA INSTITUTE OF TECHNOLOGY (1984 WORK IN PROGRESS) $\text{Ce}^{3+} - \text{Ce}^{4+}$ (SEPARATED BY TEP) S.S.F. FOR ^{140}Ce AND ^{142}Ce = 1.0001

HPLC - High-Pressure Liquid Chromatography

TCC - Thin-Layer Chromatography

S.S.F. - Stage Separation Factor

O.S.F. - Overall Separation Factor

Development of suitable calculational methods for estimating the energy consumption per separative work unit.

Comparison of the results obtained for europium with those for uranium (if available).

The proof of the existence of an isotope effect for the Eu^{2+} - Eu^{3+} system was accomplished during the first phase of the project, leading to the following modifications of the research objectives during the second phase:

The experimental confirmation of the isotopic separation factor for the Eu^{2+} - Eu^{3+} system under equilibrium and non-equilibrium (dynamic) conditions, using diethylhexyl phosphoric acid (HDEHP) for the separation of the two ionic species.

The experimental determination of exchange rates between Eu^{2+} and Eu^{3+} ions in homogeneous and heterogeneous systems.

4.2 Materials

4.2.1 Sources of Europium

Europium oxide (Eu_2O_3) 99.9% pure, obtained from Alfa Products, Danvers, MA

Europium-151 (Eu_2O_3) 96.83% isotopic purity, from ORNL

Europium-153 (Eu_2O_3) 98.75% isotopic purity from ORNL

4.2.2 Preparation of Eu^{2+}

Divalent europium oxidizes readily when contacted by air. Compounds of Eu^{2+} are not stable and fresh solutions must be prepared prior to use. Several methods were tried to prepare EuCl_2 solutions and, in one case, pure EuCl_2 crystals were separated.

4.2.2.1 Electrolytic Reduction

The glass electrolysis cell consisted of a mercury cathode, platinum anode, and a porous ceramic separator. Typical reductions were carried out under inert gas blankets (N_2 and CO_2), at a current density of $4mA/cm^2$, and europium concentrations ranging from 5 to 80 g/l. The anolyte consisted of a dilute HCl solution with a pH comparable to that of the europium solution. Reduction rates were slow, with quantitative reduction requiring four to six hours. A major advantage of this method is that no impurities are introduced. This became the preferred method during the first phase of this study.

The feasibility of Eu reduction was also demonstrated in a heterogeneous system, leading to the simultaneous transfer of the reduced Eu from an organic phase to an aqueous phase.

4.2.2.2 Reduction with Zn(Hg)

Dilute solutions of $EuCl_2$ were obtained by passing $EuCl_3$ solutions through a Jones reductor column packed with amalgamated granulated zinc. This method was exceedingly slow and was limited to dilute europium solutions. The resulting solution contained Zn, which was undesirable because of the unknown behavior of foreign ions during the isotope exchange reactions.

Concentrated solutions of $EuCl_3$ (greater than 200 g Eu/l) were contacted with amalgamated zinc granules with vigorous agitation. After filtering the solution to remove Zn(Hg), HCl

conc. was added; white crystals of $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ were formed and were washed with HCl conc. The crystals were then dissolved in distilled water. The resulting solution still contained small amounts of zinc and the high acidity interfered with subsequent solvent extraction attempts.

Eventually, satisfactory removal of Zn was obtained by treating the concentrated EuCl_2 solutions with tributyl phosphate (TBP).

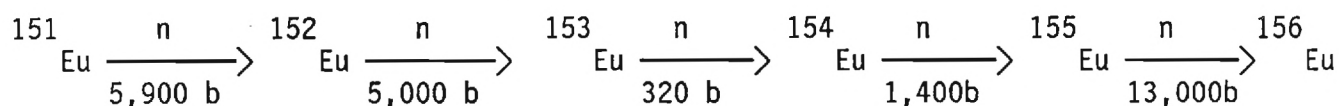
4.2.3. Neutron Activation Of Europium

Samples of natural europium oxide and also the oxides of $^{151}\text{Eu}_2\text{O}_3$ and $^{153}\text{Eu}_2\text{O}_3$ separated at the Oak Ridge Calutron were irradiated in the Georgia Tech Research Reactor. The original intent was to use gamma spectroscopy for the determination of the isotopic composition, but it became apparent that this method would not be sufficiently sensitive for small differences.

The neutron capture sequences, thermal absorption cross-sections, characteristic gamma ray energies and measured activities are shown in Table 4.

Europium tracer, obtained from the activated natural europium, was used for the determination of the distribution coefficient, kinetics studies, and for the verification of material balances.

TABLE 4

Neutron Activation of EuropiumNeutron Capture Cross-SectionsSignificant Gamma-Ray Energies

${}^{152}\text{Eu}$ ($t_{1/2} = 13.6$ years)
 ${}^{152\text{m}}\text{Eu}$ ($t_{1/2} = 9.3$ hours)
 ${}^{154}\text{Eu}$ ($t_{1/2} = 8.6$ years)

<u>E, Mev</u>	<u>Yield %</u>	<u>E, Mev</u>	<u>Yield, %</u>	<u>E, Mev</u>	<u>Yield, %</u>
0.122	28.4	0.122	7.2	0.123	40.5
0.245	7.5				
0.344	26.5				
				0.723	19.7
0.778	12.6	0.841*	14.7	0.873	11.5
0.964	14.4	0.963	12.1	0.996	10.3
1.086	9.8			1.005	17.4
1.112	13.2			1.274	35.5
1.408*	20.7				

*Energies selected for isotope assay.

Measured Activities, cpm/mg

<u>Sample</u>	<u>E = 1.408 Mev</u>	<u>E = 0.841 Mev</u>	<u>E = 1.274 Mev</u>
Natural Eu_2O_3	223.83	4.96	45.31
${}^{151}\text{Eu}_2\text{O}_3$	296.66	6.72	2.03
${}^{153}\text{Eu}_2\text{O}_3$	64.00	1.32	178.62

4.2.4. Other Reagents

Di (2-Ethylhexyl) Phosphoric Acid (DEHPA)

The technical grade product obtained from Mobil Chemical Co. was purified by several washings with ethylene glycol followed by dilute HCl.

Tributyl Phosphate - a CP grade product was obtained from Fisher Scientific.

Analytical grade reagents were used in all analytical determinations.

4.3. Analytical Methods

Eu^{3+} absorbs strongly at $394\text{m}\mu$ and this provides a convenient method for the rapid determination of Eu^{3+} and total Eu concentrations. Eu^{2+} and traces of organic solvents interfered with the determination. To obtain total europium concentration in solutions containing Eu^{2+} and Eu^{3+} ions, it is necessary to first oxidize Eu^{2+} with air. Analytical methods based on the quantitative reduction-oxidation of iron ($\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$) were particularly useful in determining Eu^{2+} and Eu^{3+} concentrations in HCl solutions containing traces of organic substances. Total Eu was determined by first reducing all the europium to Eu^{2+} with Zn-Hg, then adding excess Fe^{3+} , which resulted in quantitative reoxidation of Eu^{2+} and Eu^{3+} , and titrating the Fe^{2+} with $\text{K}_2\text{Cr}_2\text{O}_7$. Eu^{2+} determinations did not require the Zn-Hg reduction step.

Other methods explored for Eu^{2+} included precipitation of EuSO_4 and polarography.

Radioactive Eu tracer was used to obtain the relative distribution of Eu between two phases.

The isotopic ratio determination was first attempted by neutron activation and gamma spectroscopy, but it became evident that this method was not sufficiently precise to measure the small differences in isotopic composition resulting in the course of these separation studies. Eventually, mass spectrometry was employed to measure the stage separation factors. The mass spectrometric analyses were procured from AGNS and ORNL.

Chloride was determined by the classical Mohr (argentimetric) method.

4.4 Solvent Selection

Based on the studies of Peppard and coworkers²⁹, di(2-ethylhexyl) phosphoric acid (HDEHP) was believed to be suitable for the separation of Eu^{2+} and Eu^{3+} . Initial experiments in which toluene was used as a diluent were not encouraging, but substitution of dodecane eventually gave satisfactory results. The distribution coefficient for Eu^{3+} ranged between 0.2 and 100, depending on the acidity and Eu concentration (Figure 7). By contrast, Eu^{2+} did not extract ($D_{O/A} < 0.1$). Thus, the separation of Eu^{2+} and Eu^{3+} appeared possible in a continuous, countercurrent

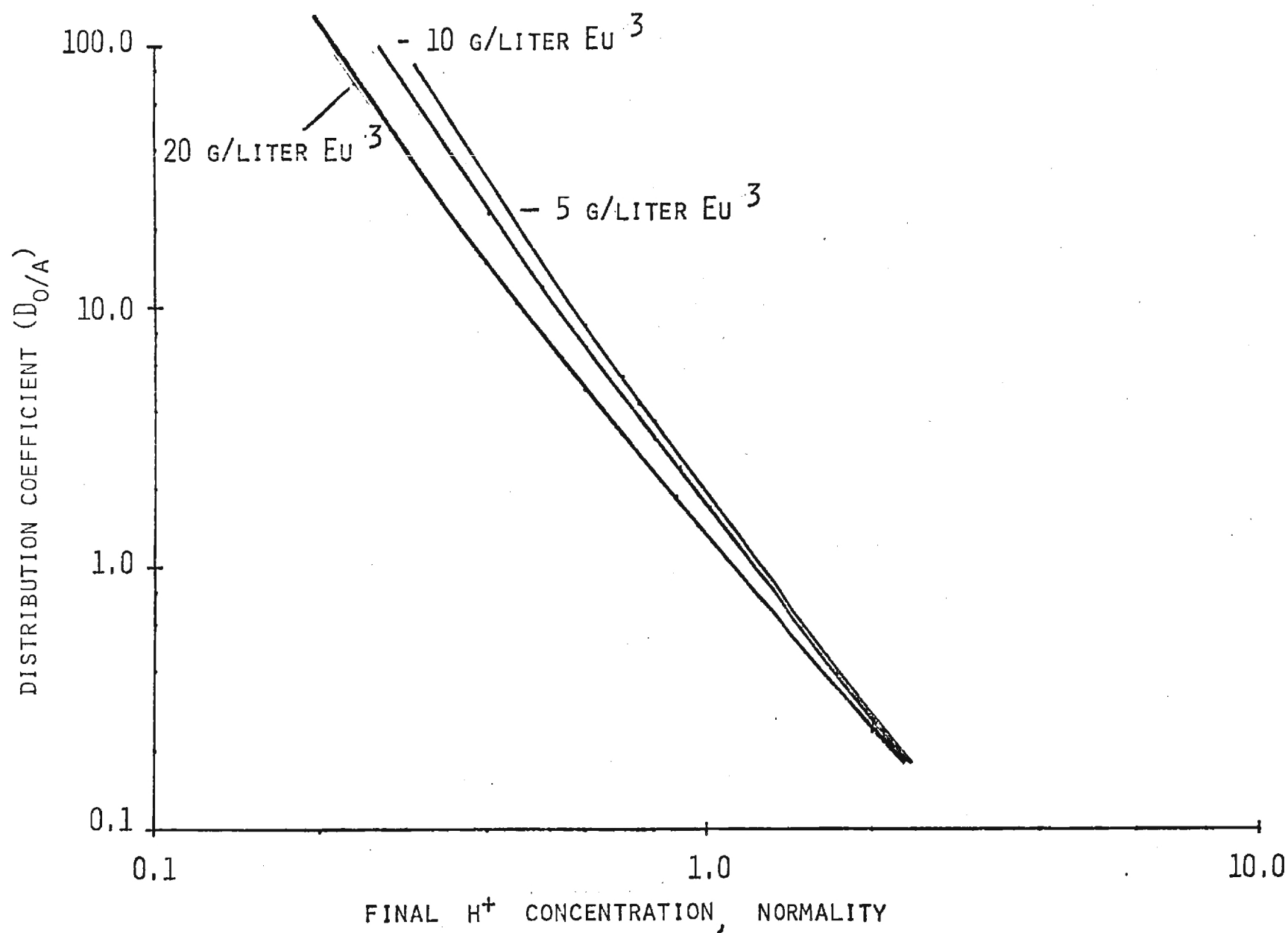


FIGURE 7. DISTRIBUTION COEFFICIENT FOR Eu^{3+} IN HDEHP/DODECANE 1/1

system. Studies of the rate of exchange between Eu^{2+} (aqueous) and Eu^{3+} (organic) have shown that, because of the very slow kinetics of this exchange, HDEHP may not be a satisfactory solvent. It is believed that the $\text{Eu}(\text{DEHP})_3$ compound present in the organic phase is too stable for a rapid exchange, which is not desirable for an efficient chemical exchange separation process. Another drawback of HDEHP is that high Eu^{3+} distributions are obtained at acidities which are very low, so that precipitation of $\text{Eu}(\text{OH})_3$ may occur at higher concentrations.

4.5 Determination Of The Isotope Separation Factor

4.5.1. Precipitation Method

4.5.1.1. Equilibrium Condition

The small stage separation factor α (see Fig. 2 for the terminology used and the quantitative relationship between the feed and stage separation factors) and the analytical limitations of mass spectrometry required multistage exchange experiments. The delays encountered with the selection of a suitable solvent led to the adoption of a selective precipitation method for simple batch cascade experiments. EuSO_4 is insoluble, while $\text{Eu}_2(\text{SO}_4)_3$ is quite soluble in dilute HCl solutions. The starting solution, containing about 50% Eu^{2+} and 50% Eu^{3+} was prepared by electrolytic reduction. Equilibration times were two to nine hours, including the time needed for the electrolytic reduction.

Five stage experiments were carried out for ^{151}Eu stripping and ^{151}Eu enriching, respectively. The experimental sequences are shown in Figures 8 and 9. In the ^{151}Eu stripping experiment, the Eu^{3+} -containing precipitate, is subjected to metathesis with Na_2CO_3 . Following oxidation with air, precipitation with NaOH , filtration, and redissolution in dilute HCl , the solution is ready for the electrolytic reduction in the following stage. In the ^{151}Eu enriching experiment, the EuSO_4 is discarded and the Eu^{3+} in the supernate is precipitated with NaOH . After redissolution with dilute HCl , the solution is electrolyzed as part of the following stage.

The feed, "heads", and "tails" solutions were converted to nitrate solutions for mass-spectrometric analyses. The results are shown in Table 5.

The stage separation factors, obtained by using the relations shown in Figure 2 are as follows:

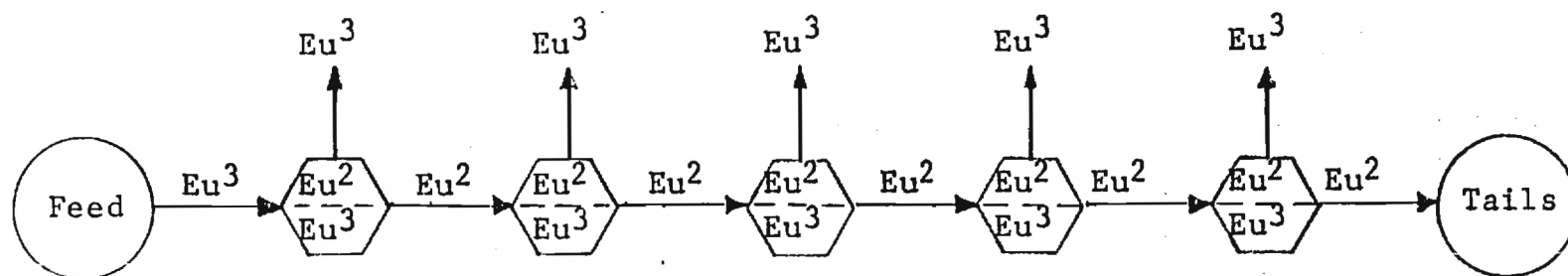
^{151}Eu Stripping Experiment:

$$\beta = 1.0003 \qquad \alpha = 1.0006 \text{ or } 1.0003 \text{ per mass number}$$

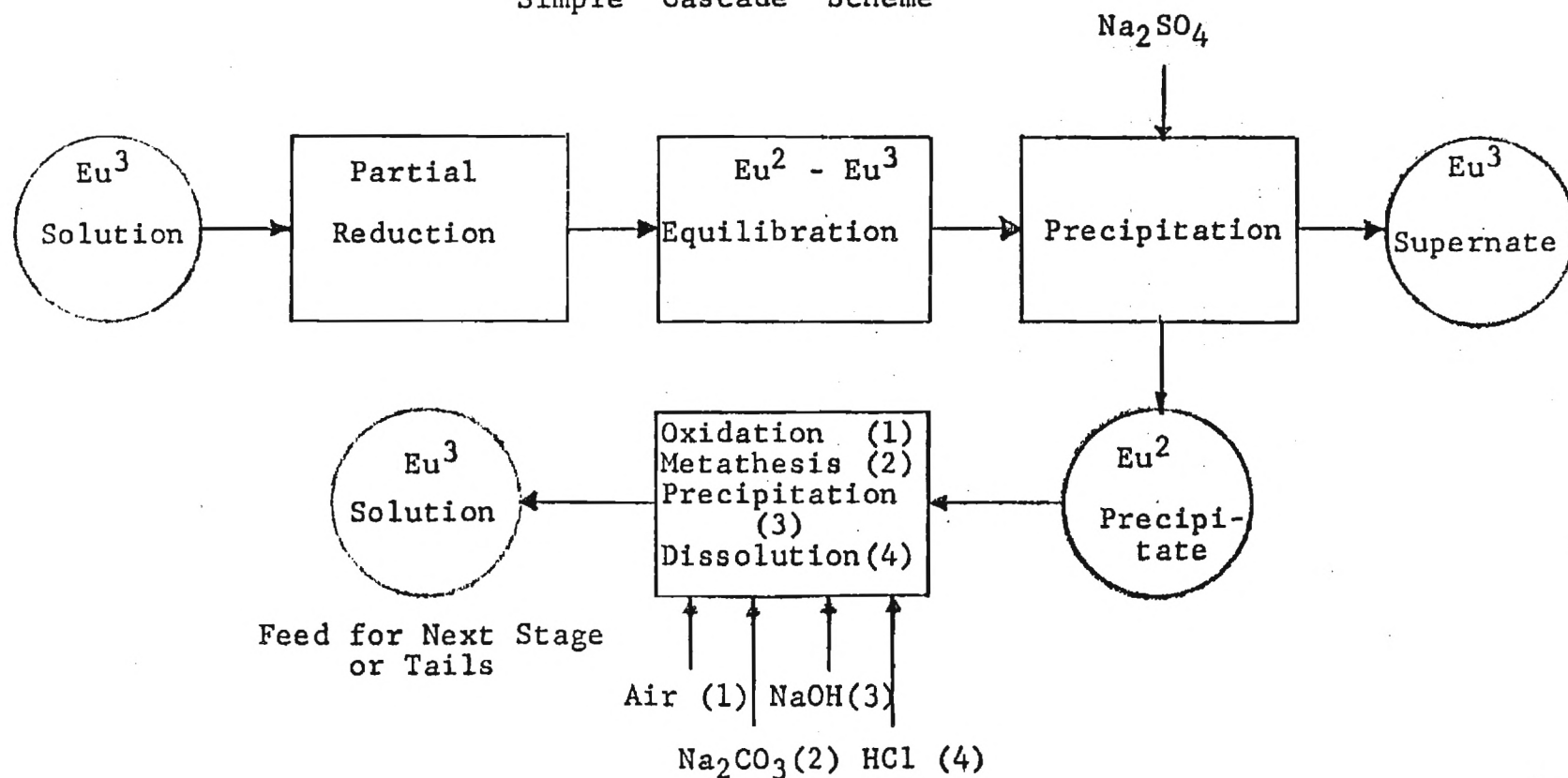
^{151}Eu Enriching Experiment:

$$\beta = 1.0003 \qquad \alpha = 1.0006 \text{ or } 1.00003 \text{ per mass number}$$

A statistical analysis of the data showed that there is less than a 0.1% probability that the results shown were due to the variability of the measurements.

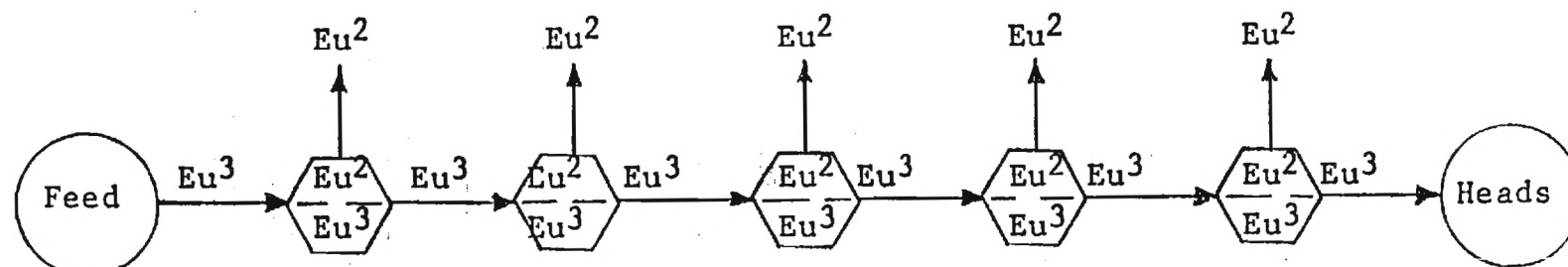


Simple Cascade Scheme

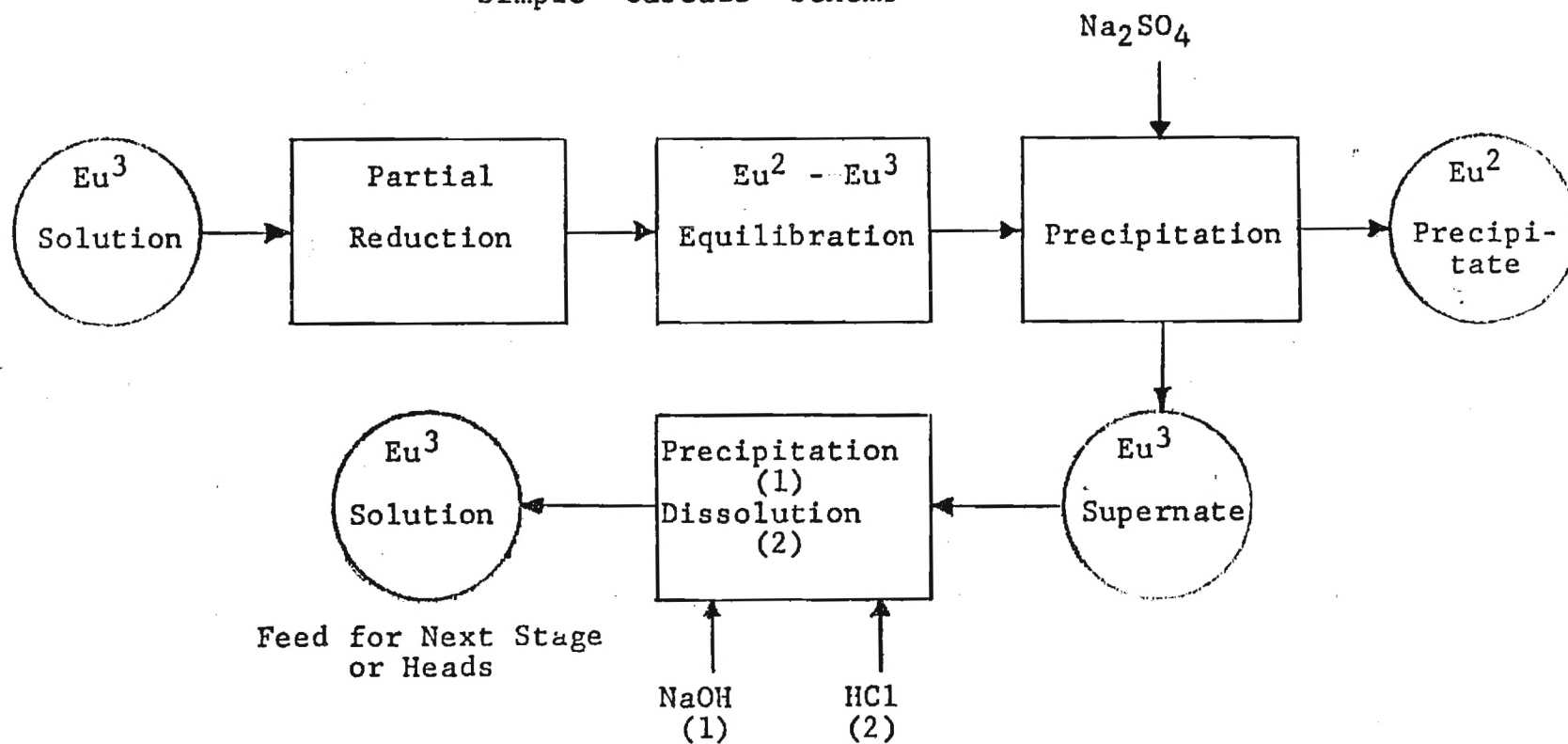


Sequence of Steps for Each Stage

Figure 8. Equilibrium Exchange Experiments -- ^{151}Eu Stripping



Simple Cascade Scheme



Sequence of Steps for Each Stage

Figure 9. Equilibrium Exchange Experiments -- ^{151}Eu Enriching

TABLE 5

EQUILIBRIUM EXCHANGE EXPERIMENTS

ANALYTICAL RESULTS

<u>Sample</u>	^{151}Eu		^{153}Eu		$\frac{^{153}\text{Eu}}{^{151}\text{Eu}}$
	x, %	σ , %	x, %	σ , %	
Feed	47.8972	0.0146	52.1028	0.0146	1.0878
Heads (Eu^{3+})	47.9299	0.0100	52.0701	0.0100	1.0864
Tails (Eu^{2+})	47.8596	0.0136	52.1404	0.0136	1.0894

4.5.1.2. Non-Equilibrium Condition

One experiment was performed to test the existence of an isotope effect during the reduction of Eu^{3+} to Eu^{2+} .

Eu^{3+} was reduced electrolytically to Eu^{2+} in the presence of SO_4^{2-} ions, which resulted in the immediate precipitation of the Eu^{2+} formed. It was shown in a preliminary experiment that the exchange rate of Eu between Eu^{3+} in solution and solid EuSO_4 is exceedingly slow. The results for the original (natural) europium and the first 2.5% to be reduced and precipitated were as follows:

^{151}Eu in original: 47.8972% with $\sigma = 0.0118\%$

^{151}Eu in precipitate: 47.9018% with $\sigma = 0.0112\%$

A statistical analysis of the data showed the difference to be insignificant.

The results indicate that a dynamic isotope effect could not be detected, but it is not possible to state that such an effect is, indeed, absent or whether the experimental procedure was not sufficiently sensitive.

4.5.2. Solvent Extraction Method

The availability of HDEHP as a selective extractant for Eu^{3+} (but not for Eu^{2+}) made it possible to test the isotope effect in the Eu^{2+} - Eu^{3+} system, as originally intended.

Batch equilibration and extraction experiments were done to simulate countercurrent extraction. Two options are available in the simulated simple cascade schemes:

The organic phases are discarded and the aqueous solutions are processed through subsequent stages, or

The aqueous phases are discarded and the organic solutions are processed through subsequent stages.

Both schemes were applied to two series of experiments: the verification of the absence of an isotope effect due only to solvent extraction and the determination of the separation factor in the system $\text{Eu}^{2+} - \text{Eu}^{3+}$. In the latter case, the two options simulate, respectively, the stripping and enriching sections of a cascade.

The experimental details are given in Figures 10-13.

In the ^{151}Eu enriching experiments, half of the Eu^{3+} in solution was reduced with Zn^{2+} to Eu^{2+} ; the two halves were equilibrated for four hours and then contacted with 1:1 HDEHP/dodecane. The aqueous phase, containing Eu^{2+} was discarded. The organic phase, containing Eu^{3+} was treated as follows:

Eu^{3+} was stripped with 4N HCl.

The solution was evaporated to dryness.

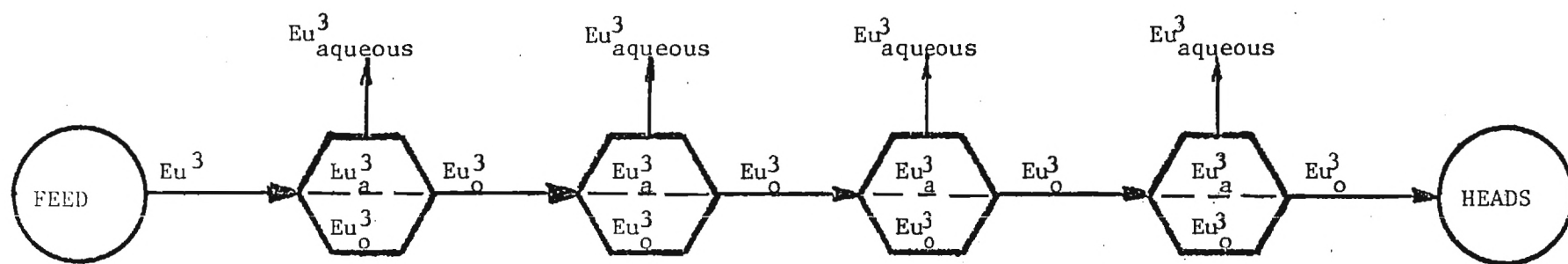
The residue was redissolved in 0.5N HCl.

The Eu^{3+} was precipitated with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and filtered.

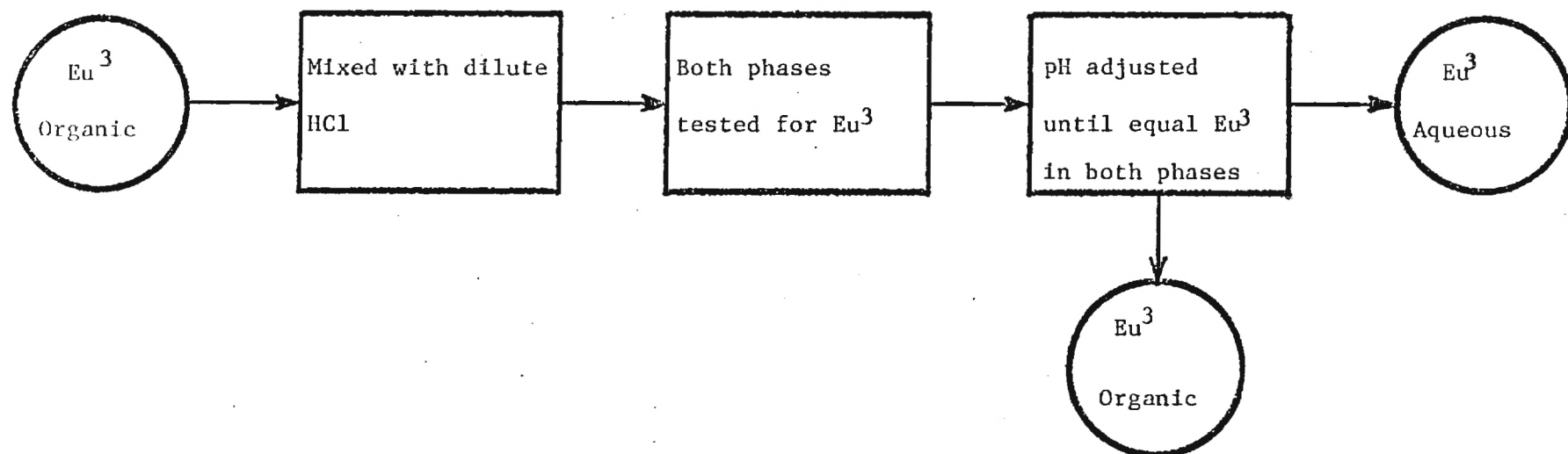
The $\text{Eu}(\text{C}_2\text{O}_4)_3$ was calcined and the resulting oxide was redissolved in 0.01N HCl.

The EuCl_3 solution is now suitable as the feed to the next "stage".

In the ^{151}Eu stripping experiments, the Eu^{2+} and Eu^{3+} solutions were prepared, equilibrated, and contacted with solvent



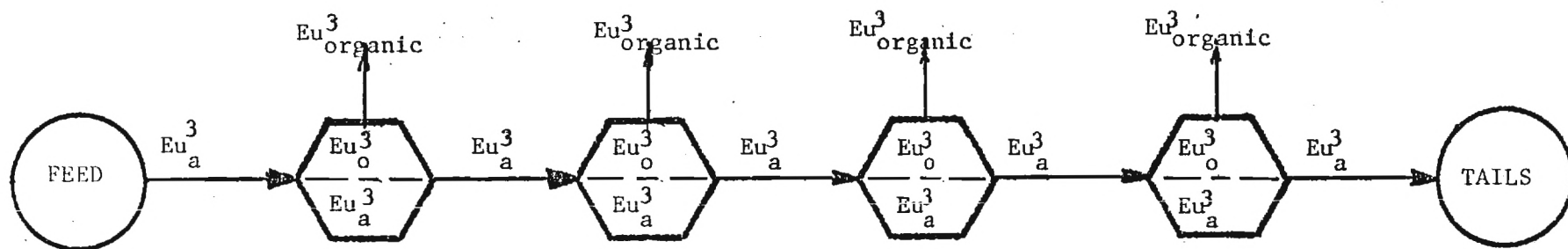
SIMPLE CASCADE SCHEME



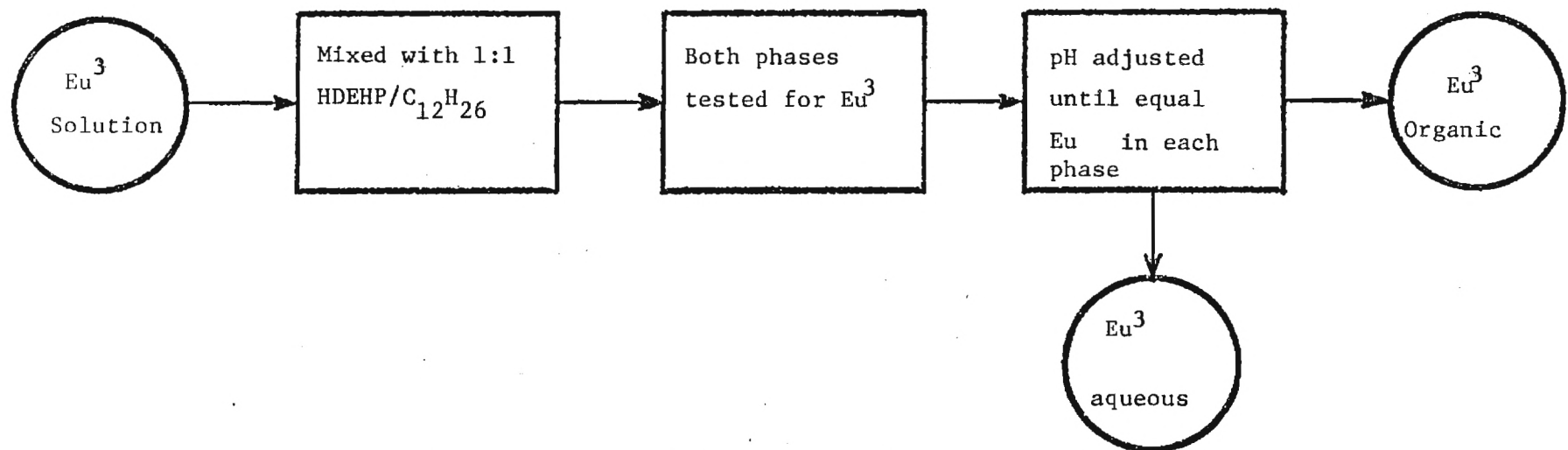
Feed for next stage or heads

Sequence of Steps for Each Stage

FIGURE 10. Test for Isotope Effect Due to Solvent Extraction



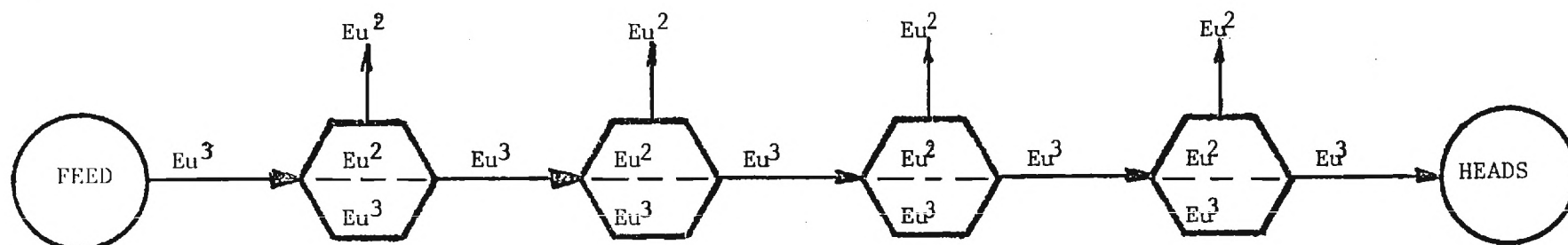
SIMPLE CASCADE SCHEME



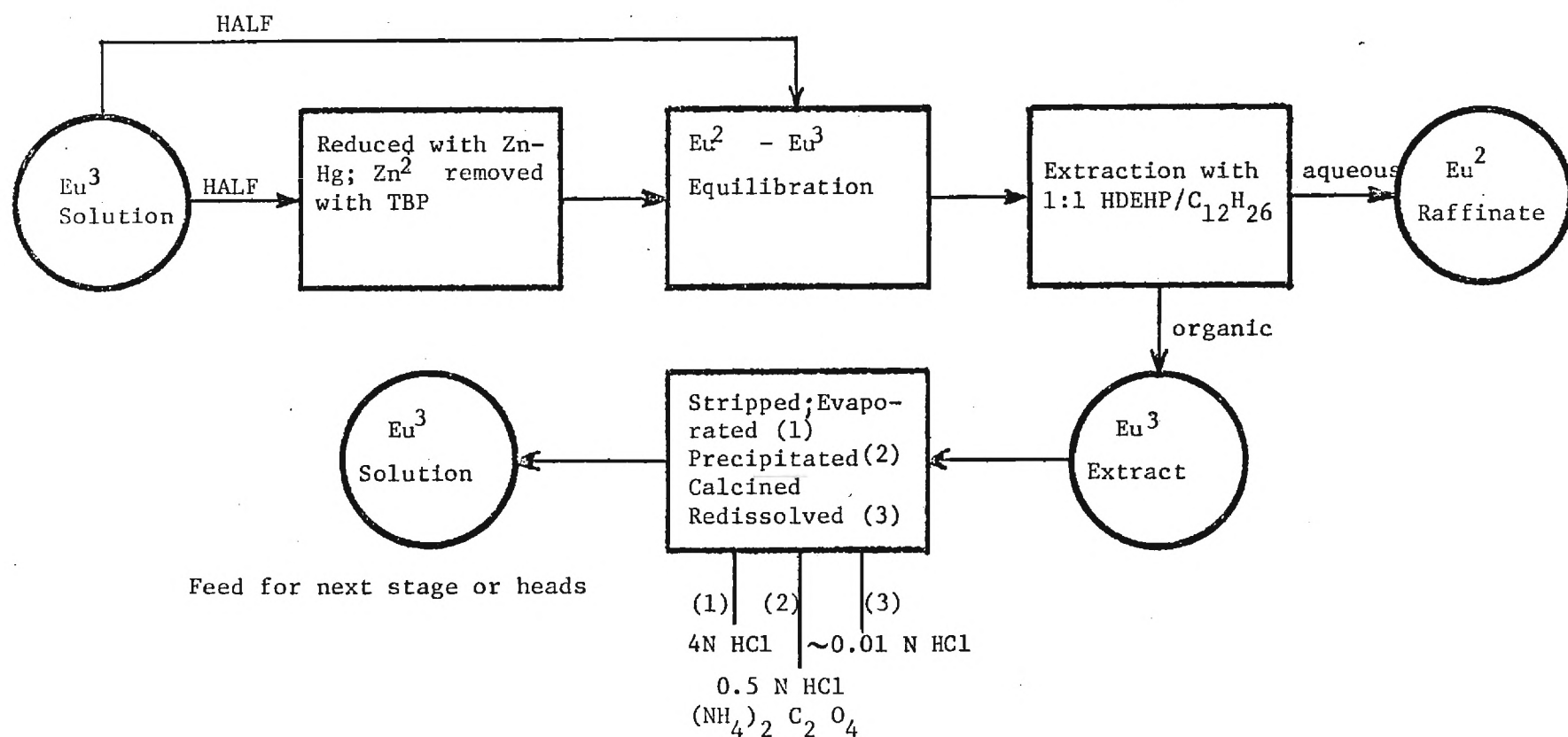
Feed for next stage or tails

Sequence of Steps for Each Stage

FIGURE 11. Test for Isotope Effect Due to Solvent Extraction

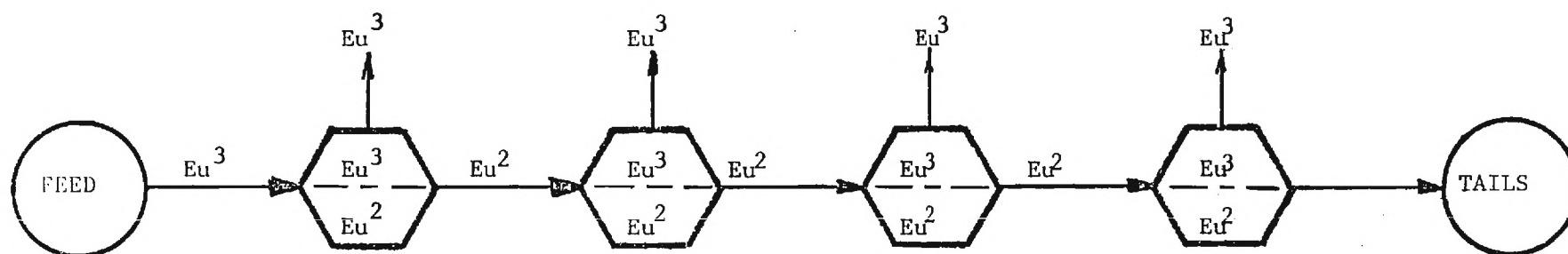


SIMPLE CASCADE SCHEME

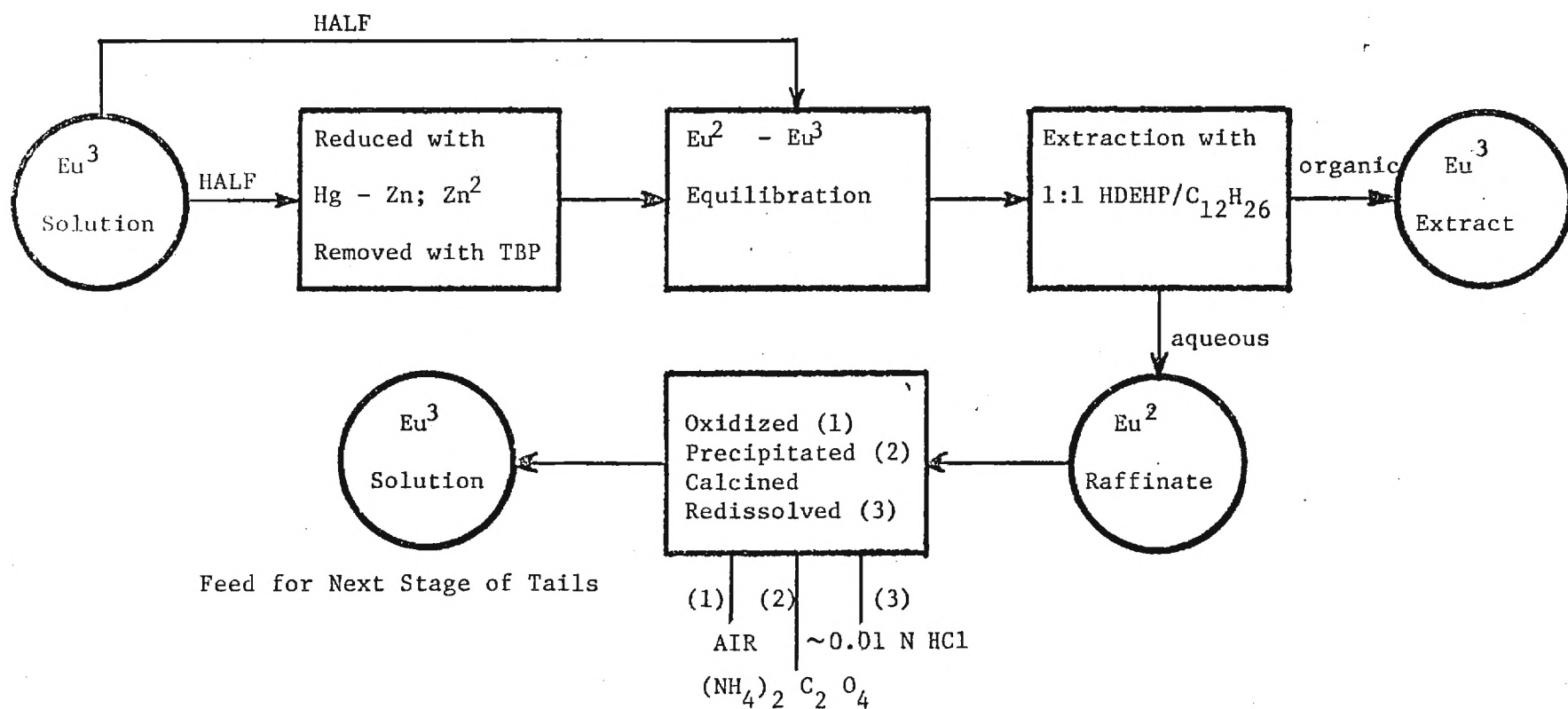


Sequence of Steps for Each Stage

FIGURE 12. EQUILIBRIUM EXCHANGE EXPERIMENTS -- ^{151}Eu ENRICHING



SIMPLE CASCADE SCHEME



Sequence of Steps for Each Stage

FIGURE 13. Equilibrium Exchange Experiments -- ^{151}Eu Stripping

the same way as above. The organic phase containing Eu^{3+} was discarded. The aqueous phase, containing Eu^{2+} , was treated as follows:

Air was bubbled through the solution to oxidize the Eu^{2+} to Eu^{3+} .

The Eu^{3+} was precipitated with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and filtered.

The $\text{Eu}(\text{C}_2\text{O}_4)_3$ was calcined and the resulting oxide was redissolved in 0.01N HCl.

The $\text{Eu}^{3+}\text{Cl}_3$ solution is now ready as the feed to the next "stage".

The difference between the $^{151}\text{Eu}/^{153}\text{Eu}$ ratios in the heads and tails solutions during the solvent effect tests were statistically not significant. It was concluded that the isotope effect in solvent extraction is either non-existent or exceedingly small in the system EuCl_3 - HDEH/ $\text{C}_{12}\text{H}_{26}$.

The equilibrium exchange experiments indicated that the stage separation factor α equals 1.0011 or 1.0005 per mass unit.

All exchange experiments results are summarized in Table 6.

4.6. Kinetics

The practicality of a continuous separation process is greatly dependent on the kinetics of the isotope exchanges involved and the transfer rates between the different phases. Separation schemes can also be optimized from exchange and transfer rate data.

TABLE 6
SUMMARY OF EXCHANGE EXPERIMENTS

EXPERIMENT	VALENCE SEPARATION METHOD	NUMBER OF STAGES	RATIO OF ¹⁵¹ Eu/ ¹⁵³ Eu		STD. DEVIATION	SEPARATION FACTOR
EQUILIBRIUM EXCHANGE	PRECIPITATION WITH SULFATE	9	HEADS	- 0.9205	0.00037	1.0006
			FEED	- 0.9193	0.00050	
			TAILS	- 0.9179	0.00049	

DYNAMIC	PRECIPITATION WITH SULFATE	1	FEED	- 0.9234	0.00044	-
			PRODUCT	- 0.9236	0.00044	

SOLVENT EFFECT	-	7	HEADS	- 0.9251	0.00064	-
			TAILS	- 0.9249	0.00095	

EQUILIBRIUM EXCHANGE	EXTRACTION WITH 1:1 HDEHP/C ₁₂ H ₂₆	7	HEADS	- 0.9207	0.0006	1.0011
			TAILS	- 0.9166	0.0006	

Radioactive europium tracer (^{152}Eu and ^{154}Eu), obtained by neutron activation of natural europium in the Georgia Tech Research Reactor, was used in all experiments. To prevent the oxidation of Eu^{2+} by air, all experiments in which Eu^{2+} was involved were done in a nitrogen filled enclosure.

4.6.1. Eu^{2+} (Aqueous) - Eu^{3+} (Aqueous) Exchange Rate

The Eu exchange rate between Eu^{2+} and Eu^{3+} ions in aqueous HCl solutions was determined for several concentrations of Eu^{2+} , Eu^{3+} , H^+ , Cl^- , and Na^+ .

A solution of EuCl_3 was divided into two equal volumes. Radioactive Eu^{3+} tracer was added to one half, while in the other half Eu^{3+} was reduced quantitatively to Eu^{2+} with a modified Jones reductor. The two solutions were then combined and mixed. After varying periods of time, aliquots were withdrawn and contacted with 1:1 HDEHP - dodecane to extract Eu^{3+} . The radioactivity of the aqueous and the organic phases was determined with a NaI scintillation detector. In addition, the Eu^{2+} free acid and chloride contents of the aqueous phase were obtained by chemical analysis. In some experiments, NaCl was added to change the ionic strength.

It was found that the exchange rate is first order with respect to Eu^{3+} , Eu^{2+} , and Cl^- concentrations and is strongly affected by the total ionic strength. The exchange is rapid at

high ionic strength, approaching a half-life of one minute. The results are shown on Figure 14.

4.6.2. Eu³⁺ (Aqueous) - Eu³⁺ (Organic) Exchange Rate

The Eu exchange rate between Eu³⁺ ions in an HCl solution and Eu³⁺ in a solution of HDEHP in dodecane (1:1) was determined under free acid conditions for which the distribution coefficient is about one. As expected, this exchange was very rapid, having a half-life of less than one minute. Exact quantitative determination was not possible with the method and equipment available, but it is obvious that this would not become an overall rate-limiting step. As in all heterogeneous exchange experiments, vigorous stirring was provided and centrifuging was used to separate the phases.

4.6.3. Eu²⁺ (Aqueous) - Eu³⁺ (Organic) Exchange Rate

The Eu exchange rate between Eu²⁺ ions contained in an HCl solution and tagged Eu³⁺ contained in a solution of HDEHP in dodecane (1:1) was studied by observing the radioactivity increase of the aqueous phase, and its decrease in the organic phase, as a function of contacting time. Exchange half-lives were very long, ranging from 103 to 163 minutes.

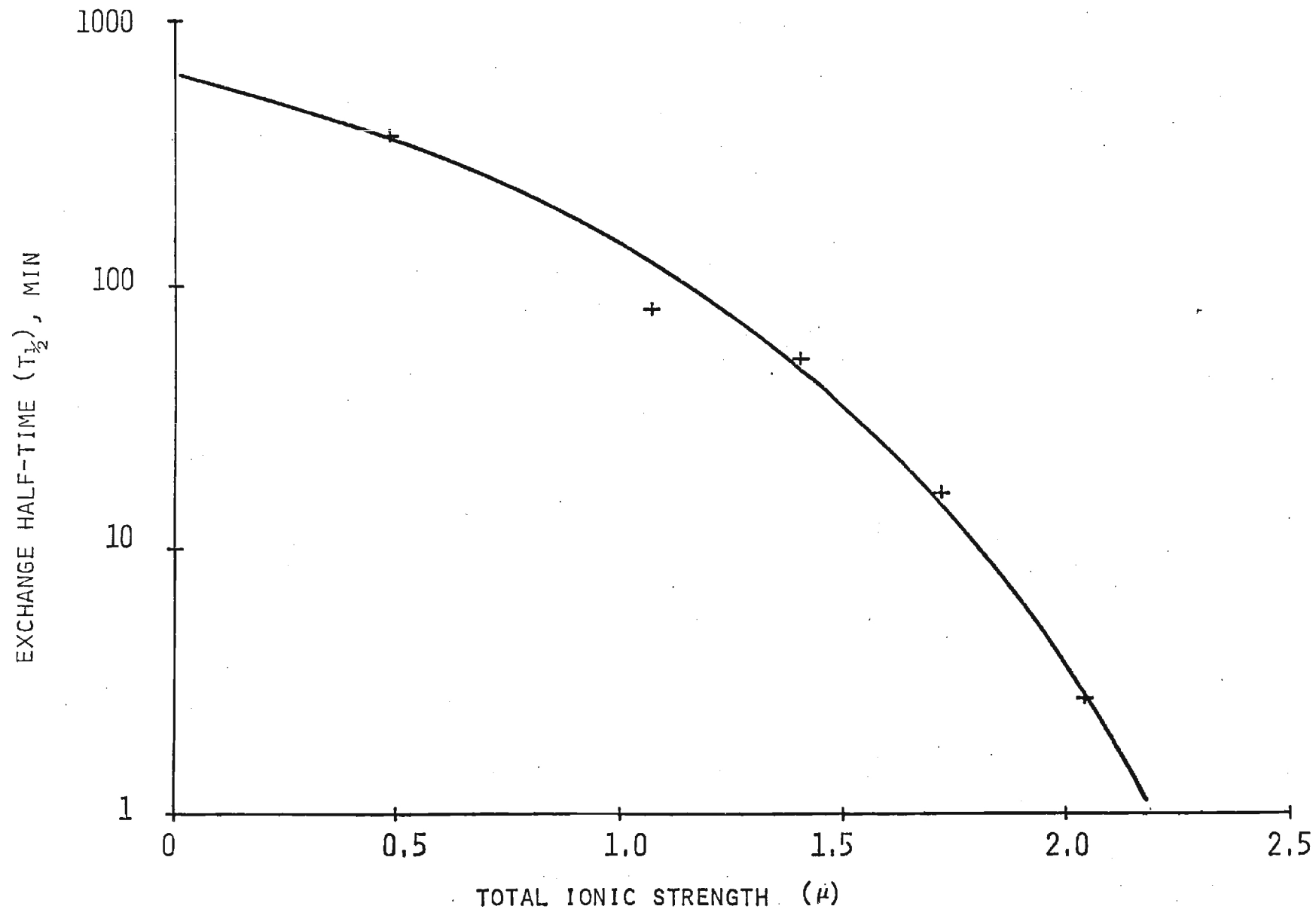


FIGURE 14. EXCHANGE HALF-TIMES BETWEEN Eu^{2+} AND Eu^{3+} IN AQUEOUS SOLUTION
AS A FUNCTION OF TOTAL IONIC STRENGTH

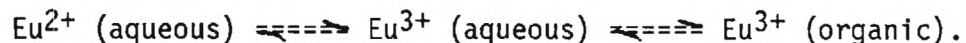
4.6.4. Eu³⁺ Extraction Rate

The transfer rate of Eu³⁺ from aqueous to organic (HDEHP/dodecane, 1:1) solution was found to be very rapid, equilibrium being attained in less than thirty seconds.

4.6.5. Process Significance Of Kinetics Results

The exchange rates appeared to be quite rapid for all cases, except for the Eu exchange rate between Eu²⁺ in an aqueous phase and Eu³⁺ in an organic phase. This was disappointing in that the simplest separation scheme, the countercurrent contacting of an organic stream containing Eu³⁺ and an aqueous stream containing Eu²⁺, does not appear practical. However, exchange rates are known to be related to the stability of the compounds in each phase and Eu(DEHP)₃, which is believed to be the Eu compound present in the organic phase, is too stable to allow for rapid isotope exchange. Other solvents (e.g., the neutral organo-phosphoric esters) which lead to the formation of moderately stable complexes will be much more suitable for this application.

Figure 15 is a schematic diagram for the three systems for which exchange rates were determined. It can be seen that the slow exchange rate between Eu²⁺ (aqueous) and Eu³⁺ (organic) can be partially overcome by the indirect exchange route



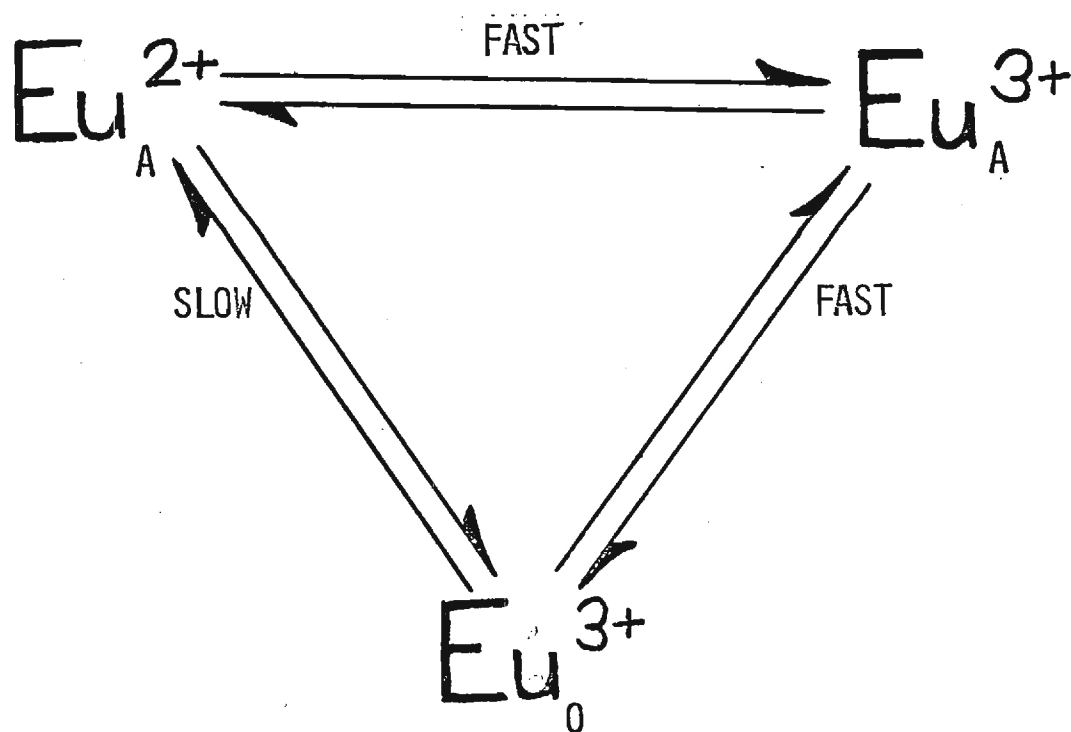


FIGURE 15. ISOTOPIC EXCHANGE RATES
 HDEHP/C₁₂H₂₆ - 1/1

This modification is achievable by a suitable adjustment of the acidity of the aqueous phase, but it will lead to a decrease of the efficiency of a single stage, thus increasing the number of stages required for a given separation.

4.7. Electrolytic Reduction In a Heterogeneous Medium

Electrochemical reductions are usually carried out in an aqueous solution with or without a separating membrane. This method worked satisfactorily for the preparation of Eu^{2+} solutions. The "electrocolumn" was developed to achieve the transfer of a solute from an organic solution by changing the valence of the dissolved element. The valence change is achieved by electrochemical reduction and the transfer from one phase to the other occurs simultaneously. This method was found to be successful for the U-Pu partitioning as part of the PUREX process for irradiated nuclear fuel reprocessing.

In the separation cascade conceptualized for the separation of Eu isotopes, the reflux at the top of the cascade requires the stripping of Eu^{3+} from the organic solution and its reduction to Eu^{2+} . This could be done in a single "electrocolumn", similar to those developed at Allied-General Nuclear Services³¹.

The feasibility for the Eu system was demonstrated in an electrolytic cell equipped with a Hg cathode, a Pt anode, porous ceramic separator, and a mechanical stirrer in the cathode compartment.

Under conditions in which complete reduction was obtained for a homogenous, aqueous solution of EuCl_3 in one hour, it was found that only 40% of the Eu contained in the organic phase was reduced and transferred to the aqueous phase.

The reasons for this limitation are not fully understood, but it appears plausible that in accordance with the Nernst Equation, the applied potential will suffice to reduce Eu^{3+} only until a given concentration ratio $(\text{Eu}^{3+})/(\text{Eu}^{2+})$ is reached. This could be remedied by either increasing the applied voltage (limited by the increase in parasitic side reactions) or by operating in a compartmentalized cell.

5. SEPARATION CASCADES

5.1. Solvent Extraction Contactors

An isotope separation cascade which could achieve varying degrees of enrichment in one Eu isotope would basically consist of counter-current solvent extraction contactors connected in series (Figure 16). The aqueous phase, containing Eu^{2+} , exits at the "bottom" of the cascade and is enriched in ^{153}Eu . The organic phase containing Eu^{3+} , emerges at the "top" of the cascade and is enriched on ^{151}Eu . The feed of natural Eu, an aqueous solution with an ionic ratio of $\text{Eu}^{3+}/\text{Eu}^{2+}$ equal to one is introduced at a suitable location. The uniqueness of this cascade, from a solvent extraction viewpoint, is the nearly constant chemical profile

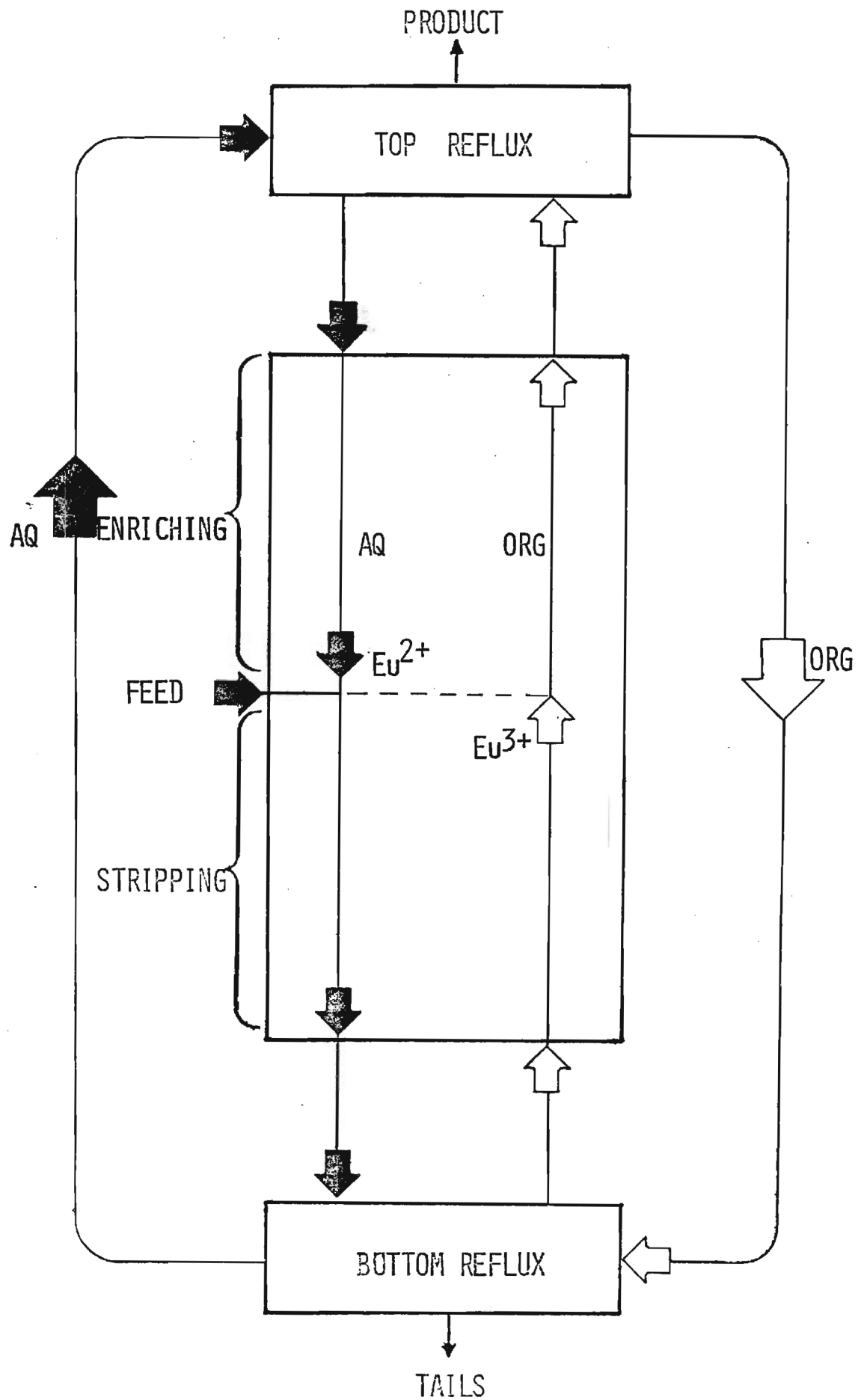


FIGURE 16. ISOTOPE SEPARATION CASCADE FOR EUROPIUM.

throughout its entire length. Of course, there will be a variation in isotopic ratio, as indicated above.

Three types of contactors were examined for this application: mixer-settlers, pulsed columns, and centrifugal contactors. The latter, while being the most advanced type, are quite expensive and amenable to more frequent maintenance outages. Mixer-settlers, shown schematically in Figure 17, have performed well in nuclear applications, but their large liquid holdup would result in a very large inventory for the cascade. Pulsed columns have also been quite useful in the reprocessing of nuclear fuel and would be quite suitable for operation in a cascade. A typical flow arrangement is shown in Figure 18.

5.2. Cascade Configuration

A countercurrent recycle cascade requires reflux at both ends. A very large saving in the total volume of liquid which would have to be circulated can be achieved by varying the reflux ratio between the feed point and the product ends, leading to a "tapered" cascade. The "ideal" cascade has a tapered configuration satisfying two conditions.

The heads separation factor β is constant.

The heads and tails stream fed to each stage have the same composition.

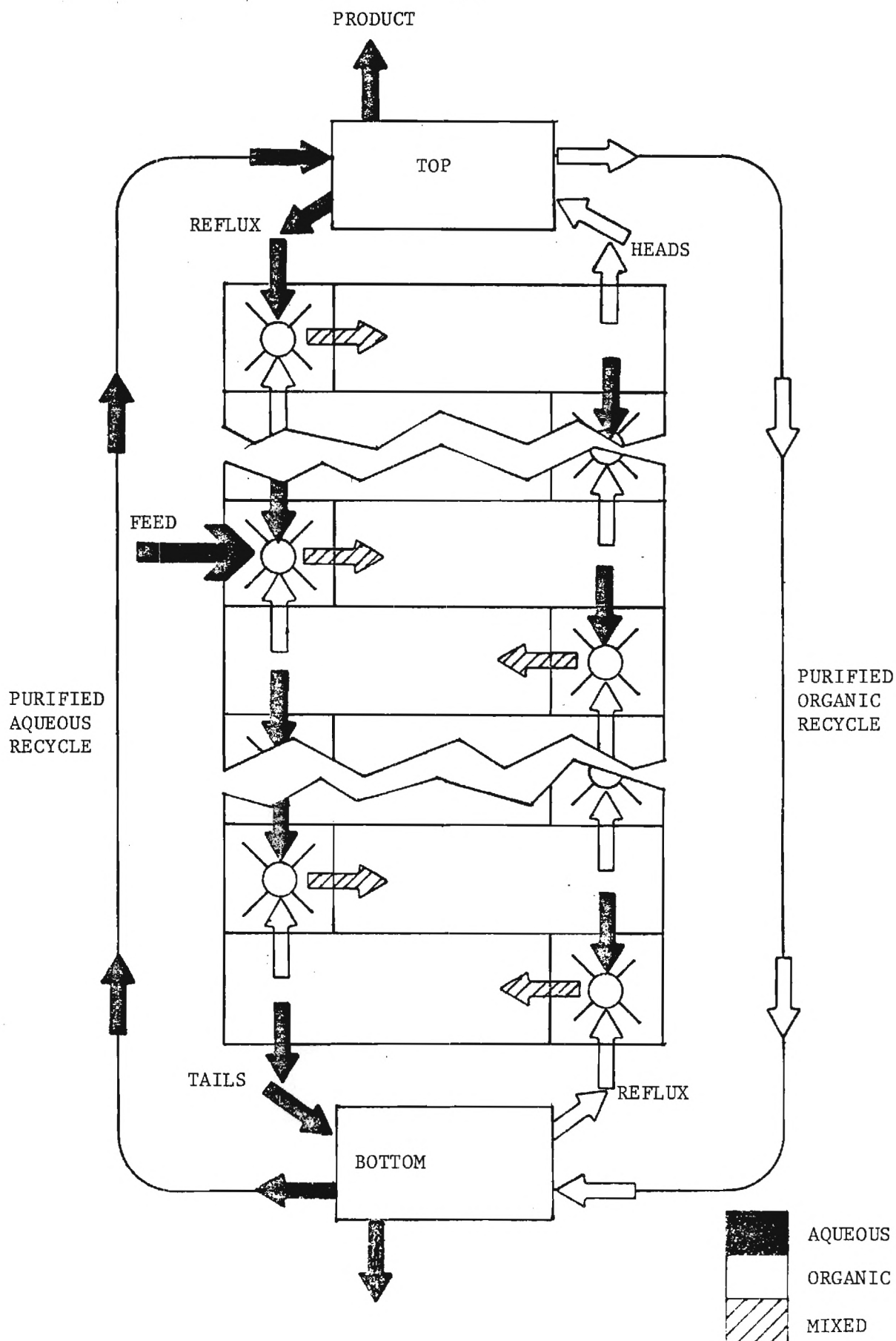


FIGURE 17. COUNTERCURRENT CASCADE OF MIXER-SETTLERS.

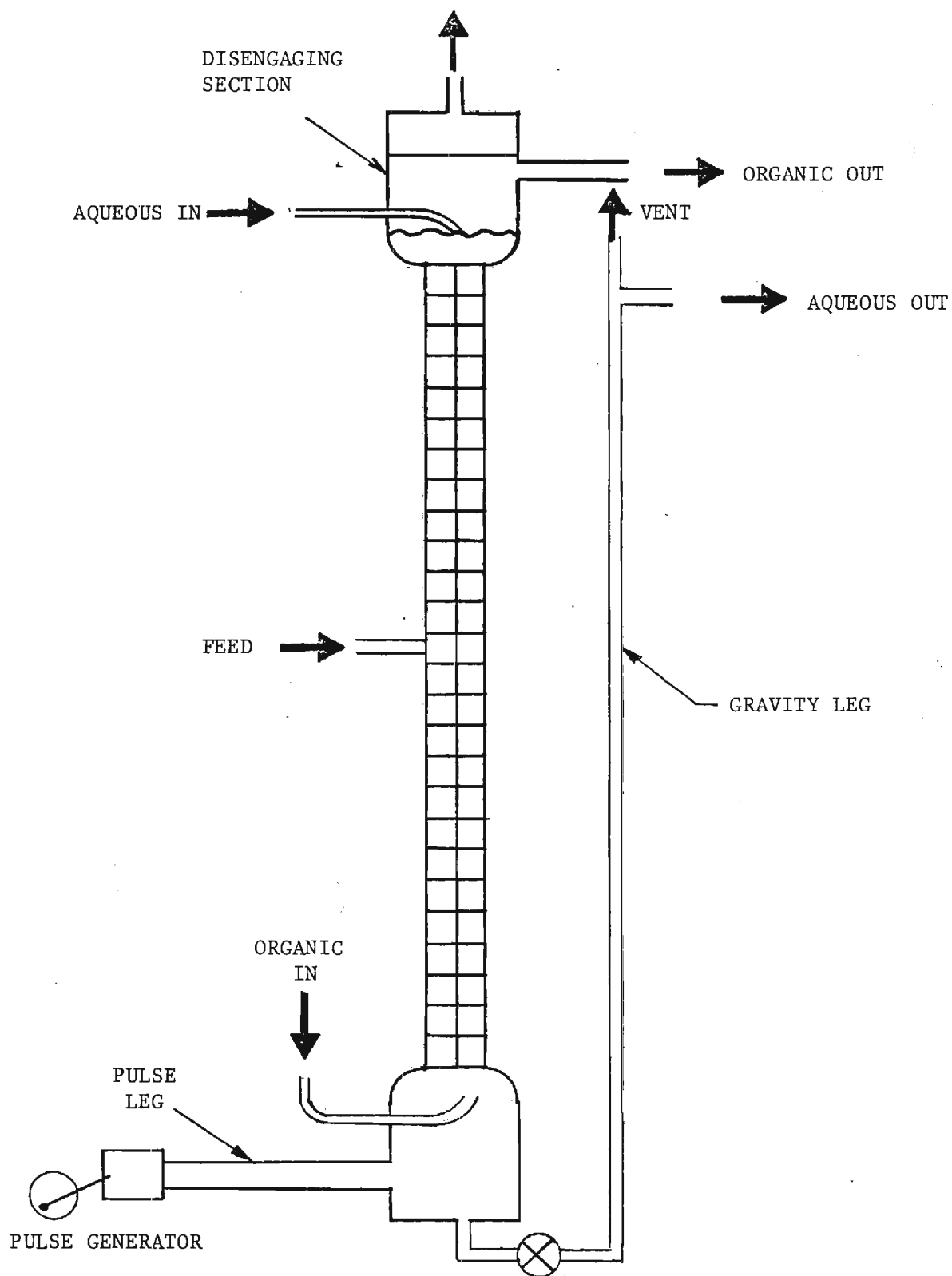


FIGURE 18. PULSE COLUMN - AQUEOUS CONTINUOUS PHASE.

Cascades approaching the "ideal" type (called "squared off") are generally used in gaseous diffusion uranium enrichment plants.

A separation cascade consisting of pulsed columns would be difficult to configure in a tapered manner, because the reflux ratio within a pulsed column remains constant. A concept whereby a larger width of the cascade is achieved in the stages around the feed point, was developed for the French CHEMEX uranium enrichment process (Figure 19)³².

5.3. Reflux Schemes

The simplest way for transferring the Eu at the bottom and top of the cascade from one phase into the other with the necessary changes in oxidation state is shown in Figures 20 and 21.

The proposed scheme approaches a closed system, with the only stream entering being the feed; the two small product streams and the excess water are the exit streams.

The largest energy output is at the top reflux where the reduction in acidity will require much thermal energy, while the reduction of Eu^{3+} to Eu^{2+} will consume appreciable electrical energy.

A novel concept was developed in the course of this study which could result in energy savings by utilizing a regenerative cell, in which some of the electric energy needed for cathodic

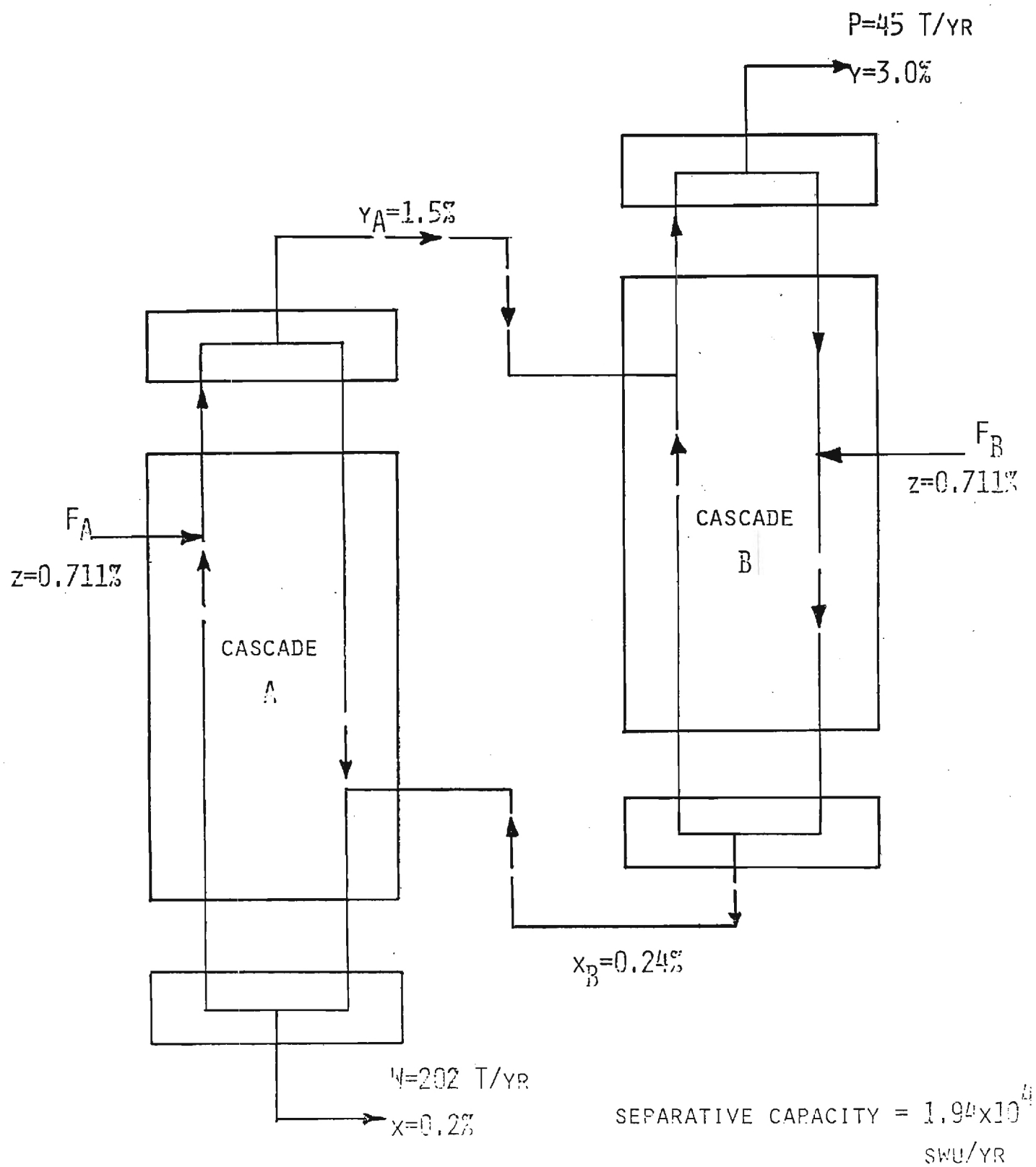


FIGURE 19. FRENCH CEA CHEMICAL EXCHANGE INDUSTRIAL MODULE

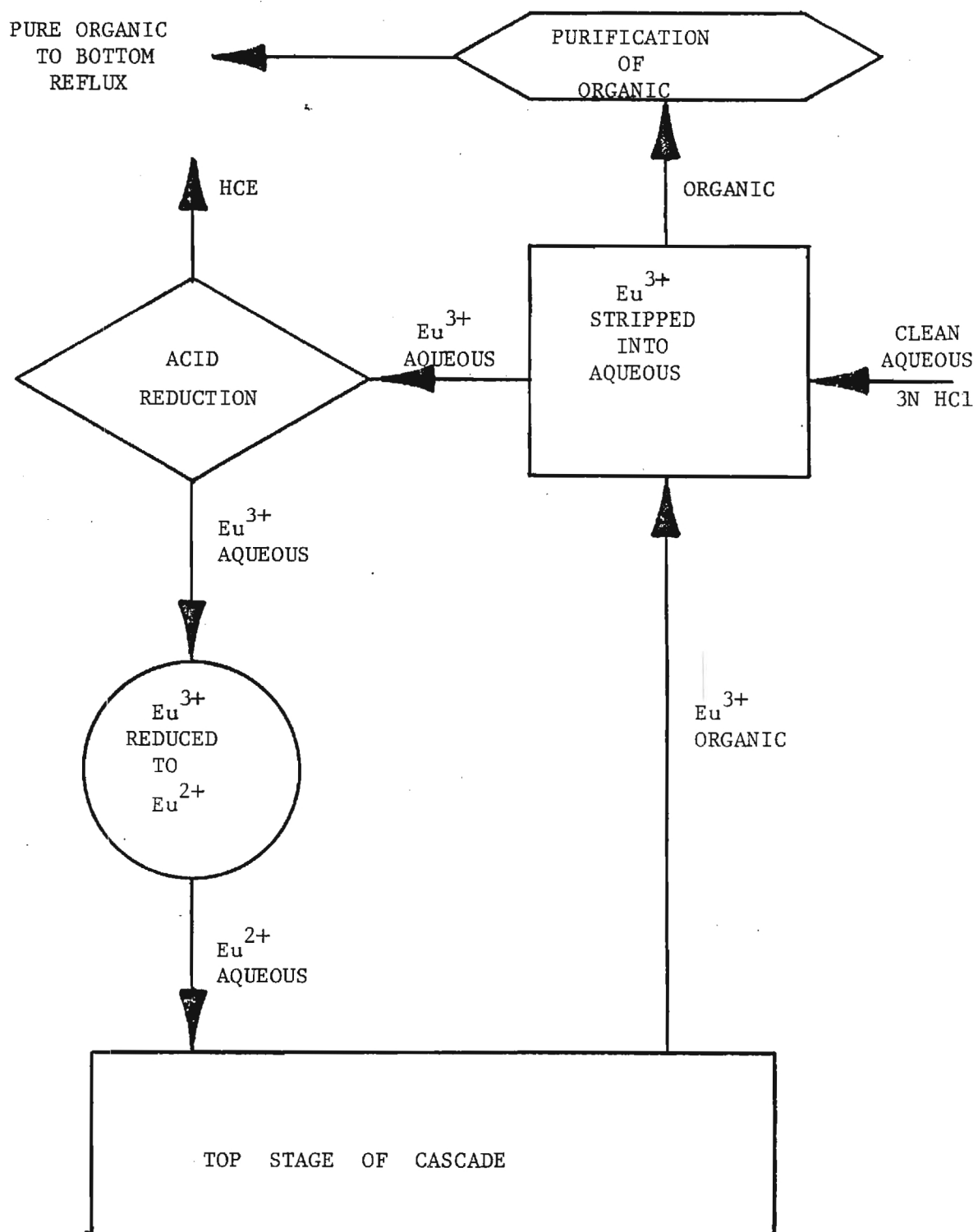


FIGURE 20. TOP REFLUX SCHEME

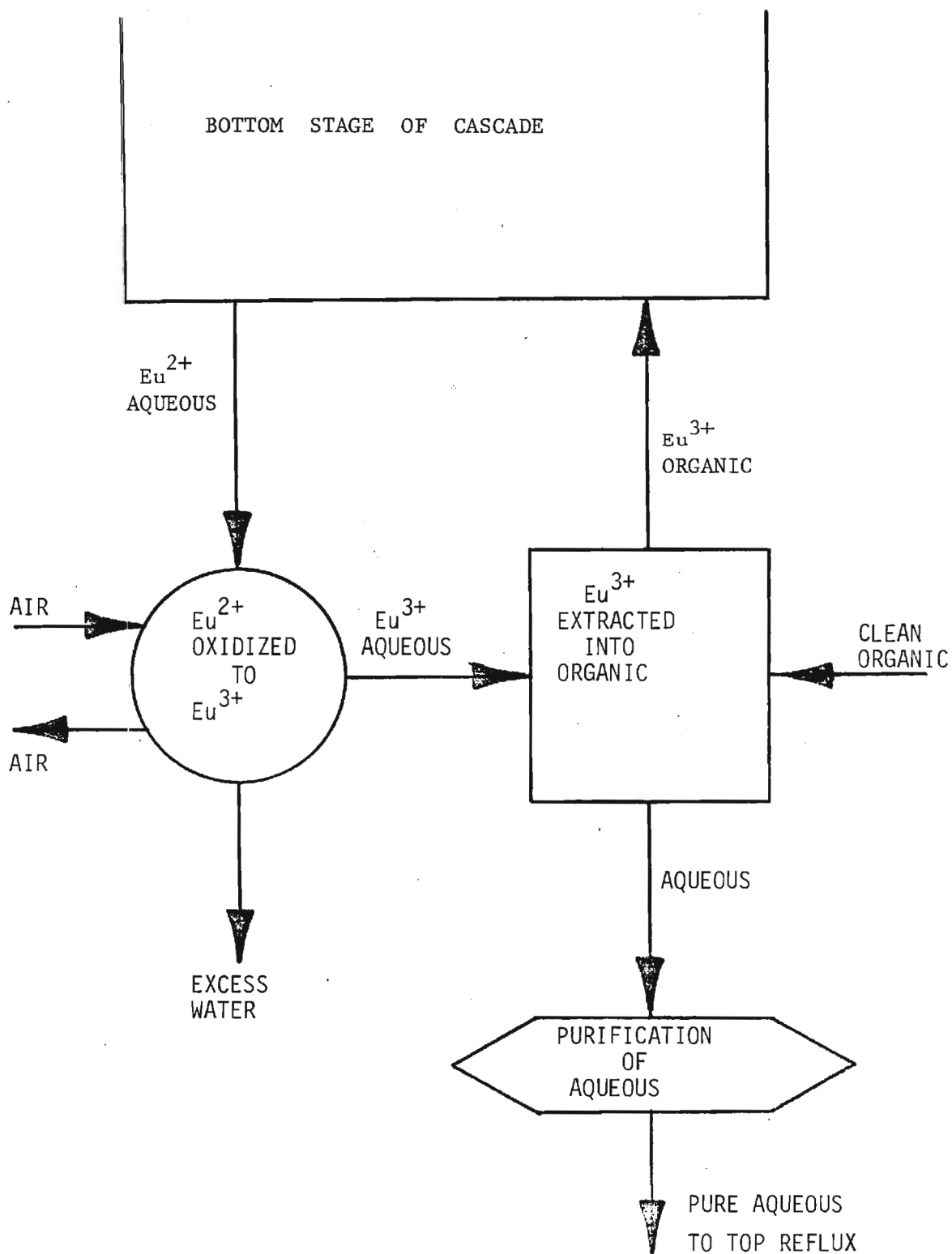


FIGURE 21. BOTTOM REFLUX SCHEME

reduction is recovered by operating the anode compartment as a fuel cell. To circumvent the eventual establishment of ionic equilibrium in both cell compartments, a heterogeneous operating mode is proposed, as shown in Figure 22. In this scheme, Eu^{3+} is recovered from the organic stream coming from the top of the cascade, reduced to Eu^{2+} in an aqueous solution and returned as reflux to the top. The Eu^{2+} aqueous stream from the bottom is oxidized in the anode compartment while generating electricity and the resulting Eu^{3+} is extracted into the organic and recycled to the bottom of the cascade. The stripped aqueous and organic liquids are circulated in opposite direction between the two compartments of the redox cell.

Near quantitative removal of Eu from the aqueous and organic streams would be necessary, since they contain the two extremes of enrichment for the cascade, and any bleeding would represent a loss in separative work.

6. CONCLUSIONS

1. $\text{Eu}^{2+}\text{Cl}_2$ was successfully prepared and solutions were found to be stable for extended periods in the absence of oxygen.
2. The existence of an isotope effect was determined in a chemical exchange reactions involving the ions Eu^{2+} and Eu^{3+} and the isotopes ^{151}Eu and ^{153}Eu .

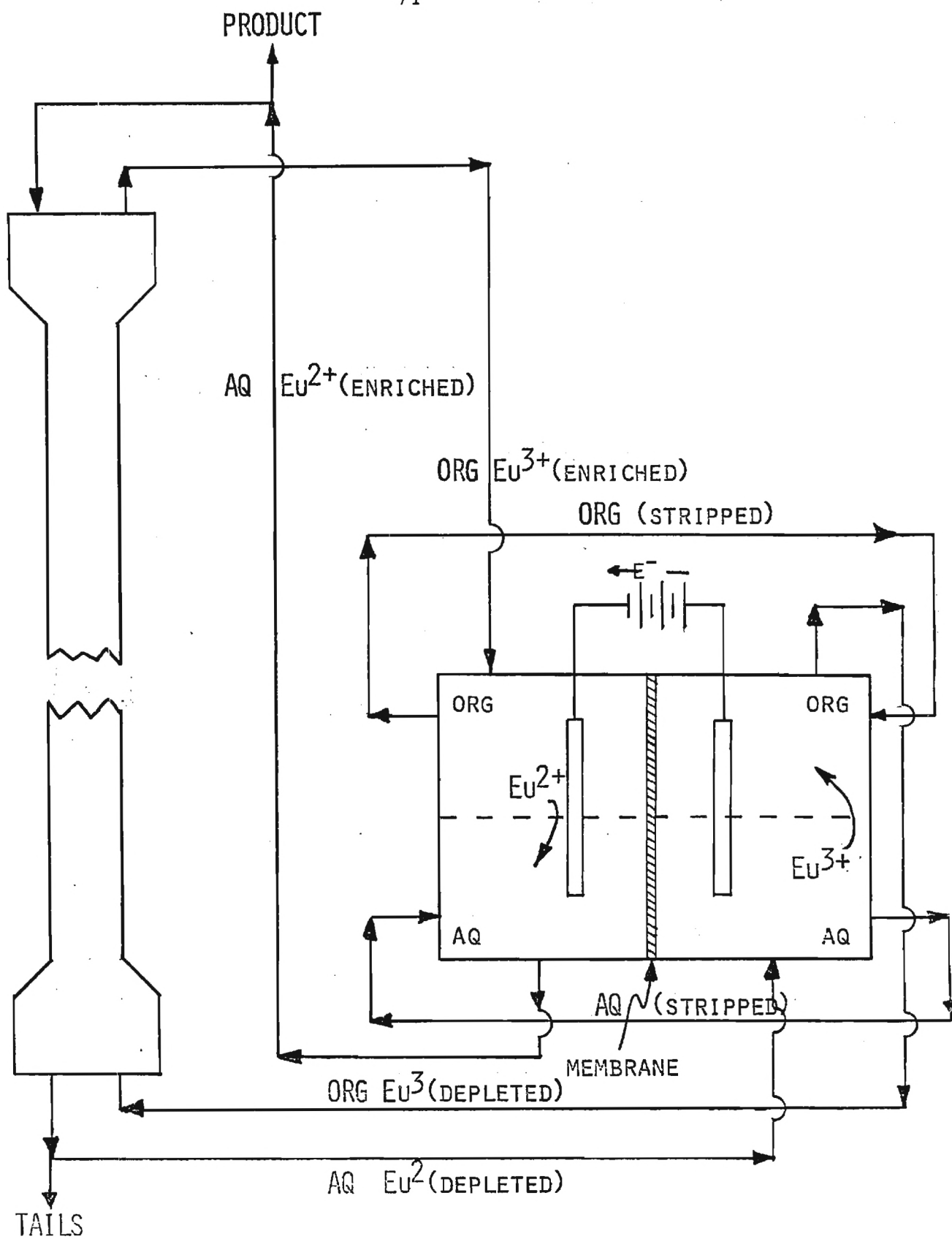


FIGURE 22. REGENERATIVE "ELECTROCELL"
FOR TOP AND BOTTOM REFLUXES

3. The single stage separation factor, α , for this exchange reaction is about 1.001 or 1.0005 per mass unit.
4. On a mass unit basis, the separation factor is of comparable magnitude as that for the exchange reactions between U^{3+} and U^{4+} and also between U^{4+} and U^{6+} .
5. The applicability of solvent extraction to a chemical exchange isotopic separation cascade was demonstrated with HDEHP. Pulse columns are the preferred contactor type.
6. The exchange rates between Eu_{aq}^{3+} and Eu_{org}^{3+} , Eu_{aq}^{2+} and Eu_{aq}^{3+} are quite rapid, but the rate for the Eu_{aq}^{2+} and Eu_{org}^{3+} is very slow. For this reason, a different solvent may have to be used.
7. The electrochemical reduction of Eu^{3+} was demonstrated in a heterogeneous system.
8. Conventional chemical reflux systems were developed for the top and bottom of a separation cascade.
9. A conceptual design was developed for reflux systems incorporating a regenerative electrochemical cell which may result in large energy savings.
10. Theoretical approaches for the estimation of separation factors in chemical exchange reactions, based on either partition functions calculations or on basic thermodynamic data, appear promising.

7.

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